Directed Vapor Deposition

A Dissertation
Presented to
the Faculty of the School of Engineering and Applied Science
University of Virginia

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy (Materials Science and Engineering)
by
James Frederick Groves
May 1998
Approval Sheet

This Dissertation is submitted in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy, Materials Science and Engineering

__________________________________________
Author, James F. Groves

This dissertation has been read and approved by the examining committee:

__________________________________________
Dissertation Advisor, H. N. G. Wadley

__________________________________________
Chairman, R. A. Johnson

__________________________________________
W. A. Jesser

__________________________________________
R. E. Johnson

__________________________________________
H. G. Wood III

__________________________________________
R. Hull

Accepted for the School of Engineering and Applied Science:

__________________________________________
Dean, School of Engineering and
Applied Science
May 1998
Abstract

This dissertation describes the invention, design, construction, experimental evaluation and modeling of a new physical vapor deposition technique (U.S. Patent #5,534,314) for high rate, efficient deposition of refractory elements, alloys, and compounds onto flat or curved surfaces. The new Directed Vapor Deposition (DVD) technique examined in this dissertation was distinct from previous physical vapor deposition techniques because it used low vacuum electron beam (e-beam) evaporation in combination with a carrier gas stream to transport and vapor spray deposit metals, ceramics, and semiconducting materials. Because of the system's unique approach to vapor phase materials processing, detailed analyses of critical concepts (e.g. the e-beam accelerating voltage and power required for evaporation, the vacuum pumping capacity necessary to generate specific gas flow velocities exiting a nozzle) were used to reduce to practice a functioning materials synthesis tool. After construction, the ability to create low contamination films of pure metals, semiconducting materials, and compounds via this new method was demonstrated, and oxide deposition using an oxygen-doped gas stream in combination with a pure metal evaporant source was shown to be feasible. DVD vapor transport characteristics were experimentally investigated with deposition chamber pressure, carrier gas type, and e-beam power being identified as major processing parameters which affected vapor atom trajectories. The low vacuum carrier gas streams employed in DVD showed a dramatic ability to focus the vapor stream during transport to the substrate and thereby enhance material deposition rates and efficiencies significantly under certain process conditions. Conditions for maximum deposition efficiency onto flat substrates and continuous fibers were experimentally identified by varying chamber pressure, carrier gas velocity (Mach number), and e-beam power. Deposition efficiencies peaked at about 0.5 Torr when coating flat or fibrous substrates. Higher Mach numbers led to higher efficiencies below the efficiency peak, but above the peak this Mach number trend reversed. Increasing e-beam power decreased the magnitude of the deposition efficiency peak and shifted it to higher chamber pressures. Fiber coating experiments revealed a maximum deposition efficiency over twice the level expected for pure line-of-sight deposition, and scanning electron microscopy revealed that, for conditions of maximum efficiency, vapor was depositing simultaneously on the
front of the fiber facing the incoming vapor and on the fiber’s sides and back. The vapor transport and deposition trends appeared to result from vapor atom collisions with gas atoms in the carrier flow, collisions which affected vapor atom form (single atom or clusters), location in the flow, and interaction with the substrate (leading to line and non-line-of-sight coating). Atomic vapor transport in DVD was investigated using Direct Simulation Monte Carlo (DSMC) methods and biatomic collision theory (BCT). For atoms transported to a flat surface perpendicular to the vapor-laden carrier gas stream, the velocity vector during transport and impact location were calculated, making possible determination of adatom deposition efficiency, spatial distribution, impact energy, and incident angle with the substrate. Model results compared favorably with random walk predictions, independent experimental data of sputter atom energy loss, and low e-beam power experimental results. The model suggested that the atoms deposited in a DVD process had a low impact energy (< 0.1 eV) and a broad incident angular distribution with the substrate. The DSMC and BCT models were used to design an improved DVD system with significantly enhanced deposition efficiency.
Where a new invention promises to be useful, it ought to be tried.

Thomas Jefferson
Acknowledgments

I thank Professor Wadley for his support throughout this research program. I trust that the results of this project fulfill his hopes and expectations for the work. I am grateful to the Defense Advanced Research Projects Agency (W. Barker, Program Manager) and NASA (D. Brewer, Technical Program Monitor) for funding this research through NASA grant NAGW 1692. The assistance of Luke Hsiung, David Hill, and Andrew Ritenour during the equipment assembly phase of this project was critical. I enjoyed the discussions Andy and I had about Directed Vapor Deposition, and I am grateful for Andy’s enthusiastic efforts which completed the DVD computer interface. While I will receive much of the credit for turning ideas into reality on this project, I know that the deposition system ultimately functioned because of the efforts of Tommy Eanes who oversaw the installation of, or installed himself, most of the major system components. Tommy’s pleasant sense of humor kept my spirits up even when things appeared to be “Not so good!” Thanks to Richard Jaurich and Rainer Bartel for professionally and patiently working to install the electron beam gun. I greatly appreciate the time Subhas Desa, Eric Abrahamson, and Sarbajit Ghosal of SC Solutions (Santa Clara, CA) invested to review the details of the dissertation’s model. Their suggestions improved the work immensely. I sincerely appreciate the countless hours my friend Paul Cantonwine has given to listening as I thought out loud about the project - all the way from Minnesota to Virginia! I am grateful to my friend Beth Duckworth for her enthusiastic support during the last several years of this project. Her tremendous energy helped me reach the finish line. Thanks to Boris Starosta for putting his artistic abilities to work to illustrate many aspects of the project. Finally, as always, I want to express my loving appreciation to my parents and to God for their unwavering support as I toiled through the many years required to bring this endeavor to completion.

James Frederick Groves
Charlottesville, Virginia
April 1998
List of Figures

Figure 1.1 Evolution of Materials Processing .............................................................. 3
Figure 1.2 Engineering materials via PVD. ............................................................... 4
Figure 1.3 Dissertation organization. ........................................................................ 9
Figure 2.1 Multicrucible e-beam deposition. ............................................................. 14
Figure 2.2 Vapor distribution in an e-beam system .................................................. 16
Figure 2.3 Vapor distribution in a high vacuum e-beam system .................................. 22
Figure 2.4 Background gas pressure modifies vapor density distribution ............... 27
Figure 2.5 The effect of clustering upon deposited film morphology ...................... 34
Figure 2.6 Molecular beam deposition .................................................................... 35
Figure 2.7 Structure of a continuum free-jet ............................................................ 38
Figure 2.8 Thornton’s zone diagram ........................................................................ 47
Figure 2.9 Vacancy concentration as a function of adatom energy ......................... 48
Figure 3.1 A preferred embodiment of Directed Vapor Deposition ...................... 51
Figure 4.1 Electron beam propagation in low vacuum ............................................ 62
Figure 4.2 Electron generating mechanism for the DVD evaporator ...................... 65
Figure 4.3 Overall e-beam gun configuration for DVD ........................................... 66
Figure 4.4 A possible e-beam scanning pattern ...................................................... 68
Figure 4.5 The electron beam system delivered from Germany .............................. 69
Figure 4.6 Chamber design facilitated simultaneous use of multiple gas streams .... 73
Figure 4.7 Pathways for reactive material deposition in DVD ................................. 74
Figure 4.8 DVD’s unique crucible design ................................................................. 75
Figure 4.9 Transfer of mechanical motion into the process chamber ...................... 77
Figure 4.10 A schematic showing the DVD system configuration ......................... 78
Figure 4.11 The graphical user interface developed for the DVD system ............... 86
Figure 4.12 Object-oriented programming for the DVD computer interface .......... 87
Figure 4.13 The assembled DVD system in the laboratory ..................................... 89
Figure 5.1 The general DVD system configuration for all experiments described ... 91
Figure 5.2 Available processing range (Mach number vs. chamber pressure) ......... 93
Figure 5.3 Available processing range (Mach number vs. carrier gas flux) .......... 94
Figure 5.4 Available processing range for argon / helium using a 1.27 cm nozzle .... 95
Figure 5.5 Initial system configuration for flow visualization ................................. 98
Figure 5.6 Gas flow structure ................................................................................. 101
Figure 5.7 Vapor entrainment into carrier gas fluxes .............................................. 104
Figure 5.8 Constant carrier gas flux ....................................................................... 107
<p>| Figure 5.9 | Constant chamber pressure. |
| Figure 5.10 | Effect of e-beam power variations in helium |
| Figure 5.11 | Effect of e-beam power variations in argon |
| Figure 5.12 | Flow interactions with substrates and crucible |
| Figure 6.1 | System configuration for material synthesis experiments |
| Figure 6.2 | An Auger electron spectroscopy scan of DVD deposited copper |
| Figure 6.3 | Optical absorption coefficient analysis of DVD deposited silicon |
| Figure 7.1 | The general dimensions of all deposition efficiency experiments |
| Figure 7.2 | Flat substrate deposition efficiency as a function of chamber pressure and Mach number |
| Figure 7.3 | Two distinct regions of material deposit for high gas flows |
| Figure 7.4 | Formation of a deposition halo at high gas flows |
| Figure 7.5 | The effect of e-beam power upon deposition efficiency |
| Figure 7.6 | Crucible to nozzle separation effects upon deposition efficiency |
| Figure 7.7 | Effect of initial vapor distribution upon deposition efficiency |
| Figure 7.8 | Material utilization efficiency during DVD fiber coating |
| Figure 7.9 | Evidence of non line-of-sight coating |
| Figure 7.10 | Vapor density distribution during transport |
| Figure 7.11 | Scenarios to explain the effect of clustering upon deposit appearance |
| Figure 7.12 | Cluster probability as a function of process conditions |
| Figure 8.1 | Vapor transport modeling of DVD |
| Figure 8.2 | A flowchart summary of Bird’s DSMC code |
| Figure 8.3 | An overlay of the DSMC modeling grid onto the experimental setup |
| Figure 8.4 | Specifications for the DSMC modeling grid |
| Figure 8.5 | The computational flow of the BCT code |
| Figure 8.6 | Calculation of the initial vapor atom trajectory |
| Figure 8.7 | Spatial distribution of deposited vapor |
| Figure 8.8 | Impact parameter / deflection angle vs. energy of collision event |
| Figure 8.9 | Log-linear fits for ( \chi_{\text{cutoff}} ) |
| Figure 8.10 | Summary of steps required to determine atomic mean free path ( \lambda ) |
| Figure 8.11 | Parameters factoring into a collision calculation |
| Figure 8.12 | Determination of the post-collision velocity vector |
| Figure 8.13 | Steps to compute new vapor atom velocity vector after a collision |
| Figure 9.1 | Comparison of flowfield simulation with experimental result |
| Figure 9.2 | Random walk on an atomic surface |
| Figure 9.3 | Persistent random walk during vapor phase diffusion |</p>
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 9.4</td>
<td>Pure vs. persistent random walk.</td>
</tr>
<tr>
<td>Figure 9.5</td>
<td>Energy distribution of atoms leaving a sputtering target.</td>
</tr>
<tr>
<td>Figure 9.6</td>
<td>Energy loss at 2.5 cm.</td>
</tr>
<tr>
<td>Figure 9.7</td>
<td>Energy loss at 5.0 cm.</td>
</tr>
<tr>
<td>Figure 10.1</td>
<td>Vapor atom transport at low chamber pressure.</td>
</tr>
<tr>
<td>Figure 10.2</td>
<td>Vapor atom transport at intermediate chamber pressure.</td>
</tr>
<tr>
<td>Figure 10.3</td>
<td>Vapor atom transport at high chamber pressure.</td>
</tr>
<tr>
<td>Figure 10.4</td>
<td>Vapor atom energy during transport.</td>
</tr>
<tr>
<td>Figure 10.5</td>
<td>Vapor atom orientation during transport.</td>
</tr>
<tr>
<td>Figure 10.6</td>
<td>Flowfield temperature profile at intermediate chamber pressure.</td>
</tr>
<tr>
<td>Figure 10.7</td>
<td>Chamber pressure variation at intermediate pressure.</td>
</tr>
<tr>
<td>Figure 10.8</td>
<td>Predicted deposition efficiency trends with chamber pressure.</td>
</tr>
<tr>
<td>Figure 10.9</td>
<td>Effect of dilute limit approximation upon modeling results.</td>
</tr>
<tr>
<td>Figure 10.10</td>
<td>Distributions of impact energies for various conditions.</td>
</tr>
<tr>
<td>Figure 10.11</td>
<td>Distributions of impact angle for various conditions.</td>
</tr>
<tr>
<td>Figure 10.12</td>
<td>Simulated vapor distributions.</td>
</tr>
<tr>
<td>Figure 10.13</td>
<td>Line scans across simulated thickness profiles.</td>
</tr>
<tr>
<td>Figure 11.1</td>
<td>A reconfigured DVD system.</td>
</tr>
<tr>
<td>Figure 11.2</td>
<td>Grid for modeling of reconfigured system.</td>
</tr>
<tr>
<td>Figure 11.3</td>
<td>Close-up of reconfigured system.</td>
</tr>
<tr>
<td>Figure 11.4</td>
<td>Simulation of vapor transport in the reconfigured system.</td>
</tr>
<tr>
<td>Figure 11.5</td>
<td>Nozzle geometry can affect gas focus.</td>
</tr>
<tr>
<td>Figure 12.1</td>
<td>Multicrucible vapor stream mixing in DVD.</td>
</tr>
<tr>
<td>Figure A.1</td>
<td>Wehnelt cup assembly which generates the e-beam.</td>
</tr>
<tr>
<td>Figure A.2</td>
<td>Overview drawing of traditional components of DVD e-beam gun.</td>
</tr>
<tr>
<td>Figure A.3</td>
<td>Beam Generating Assembly, top portion of DVD e-beam gun.</td>
</tr>
<tr>
<td>Figure A.4</td>
<td>Beam Guidance System, center section of DVD e-beam gun.</td>
</tr>
<tr>
<td>Figure A.5</td>
<td>Pressure Decoupling Chamber, bottom section of DVD e-beam gun.</td>
</tr>
<tr>
<td>Figure A.6</td>
<td>Stainless steel processing chamber with 2.54 cm thick walls.</td>
</tr>
<tr>
<td>Figure A.7</td>
<td>Specially designed DVD water-cooled crucible.</td>
</tr>
<tr>
<td>Figure A.8</td>
<td>Estimation of chamber pumping requirements.</td>
</tr>
<tr>
<td>Figure A.9</td>
<td>Achievable gas flow velocity for various pumping configurations.</td>
</tr>
<tr>
<td>Figure B.1</td>
<td>Cluster size as a function of time.</td>
</tr>
<tr>
<td>Figure E.1</td>
<td>Distribution of Ti-6-4 on substrate located directly above evaporant.</td>
</tr>
<tr>
<td>Figure E.2</td>
<td>Ti-6-4 distribution on substrate directly above evaporant.</td>
</tr>
</tbody>
</table>
# List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Thermophysical data</td>
<td>59</td>
</tr>
<tr>
<td>4.2</td>
<td>Computer interface information for DVD system components</td>
<td>85</td>
</tr>
<tr>
<td>6.1</td>
<td>DVD deposition of silicon</td>
<td>125</td>
</tr>
<tr>
<td>7.1</td>
<td>Deposition efficiency of copper onto flat substrate</td>
<td>134</td>
</tr>
<tr>
<td>7.2</td>
<td>Deposition efficiency of copper as a function of e-beam power</td>
<td>144</td>
</tr>
<tr>
<td>7.3</td>
<td>Deposition efficiency of copper onto flat substrate</td>
<td>149</td>
</tr>
<tr>
<td>7.4</td>
<td>Deposition efficiency of copper onto stationary fibers</td>
<td>154</td>
</tr>
<tr>
<td>7.5</td>
<td>Variation of clustering probability with process conditions</td>
<td>161</td>
</tr>
<tr>
<td>8.1</td>
<td>Knudsen numbers for extreme experimental conditions</td>
<td>169</td>
</tr>
<tr>
<td>8.2</td>
<td>User-configurable DSMC model parameters</td>
<td>176</td>
</tr>
<tr>
<td>8.3</td>
<td>Required inputs for bimolecular collision theory model</td>
<td>179</td>
</tr>
<tr>
<td>9.1</td>
<td>Copper atom energy 2.5 cm from target</td>
<td>209</td>
</tr>
<tr>
<td>9.2</td>
<td>Copper atom energy 5.0 cm from target</td>
<td>209</td>
</tr>
<tr>
<td>10.1</td>
<td>Number of grid points used for each chamber pressure</td>
<td>213</td>
</tr>
<tr>
<td>10.2</td>
<td>DVD process simulation results</td>
<td>225</td>
</tr>
<tr>
<td>11.1</td>
<td>Enhanced DVD deposition characteristics</td>
<td>241</td>
</tr>
<tr>
<td>E.1</td>
<td>Deposited vapor thickness versus location</td>
<td>349</td>
</tr>
</tbody>
</table>
List of Symbols

\( a \) Specific evaporation rate
\( a_u \) Born radius (0.529 Å)
\( A \) An individual atom
\( A_2 \) Two atom cluster
\( A_3 \) Three body cluster
\( A_n \) Cluster containing n atoms
\( A_{n-1} \) Cluster containing n-1 atoms
\( A_{pipe} \) Area of the inlet flow tube
\( b \) Impact parameter
\( b_{max} \) Maximum range of interaction of atoms involved in a collision event
\( B \) Beam energy
\( B_o \) Initial beam energy
\( c \) Speed
\( \bar{c} \) Average speed
\( [Cu] \) Concentration of metal monomer
\( [Cu_2^*] \) Concentration of unstable dimers
\( d \) Diameter
\( d_s \) Local film thickness on a flat substrate
\( d_{so} \) Maximum film thickness
\( D \) Distance
\( e \) Binary collision encounters
\( e \) Charge on an electron
\( E \) Kinetic energy
\( f \) Velocity distribution function
\( F \) External force
\( h \) Thickness
List of Symbols

$h_v$ Source to substrate separation distance
$H$ Total Enthalpy
$\Delta H$ Enthalpy
$[He]$ Concentration of background gas
$I$ Intensity
$I$ Beam current
$I_o$ Initial intensity
$k$ Boltzmann’s constant (1.381x10^{-23} J/K)
$Kn$ Knudsen number
$l$ Atomic jump distance on crystal surface
$L$ Characteristic dimension of a modeled volume
$n$ Exponent in vapor density distribution function
$n$ Gas atom number density
$n$ Number of jumps
$N$ Number of molecules in an ensemble
$m$ Mass
$m_c$ Carrier gas atom mass
$m_v$ Vapor atom mass
$M$ Three-body collision partner
$M$ Mach number
$M^*$ Energized third member of cluster collision event
$n_o$ Direction unit vector
$N_A$ Avogadro’s number (6.0221x10^{23} atoms/mol)
$N_{av}$ Average size of clusters
$P$ Pressure
$P_c$ Carrier gas pressure
$P_{collision}$ Probability of a collision
$P_d$ Downstream pressure at a nozzle or inside a processing chamber
$P_o$ Upstream pressure before a nozzle
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_s$</td>
<td>Saturated vapor pressure</td>
</tr>
<tr>
<td>$q$</td>
<td>Direction vector</td>
</tr>
<tr>
<td>$q$</td>
<td>Heat flux</td>
</tr>
<tr>
<td>$r$</td>
<td>Distance between atoms</td>
</tr>
<tr>
<td>$r_{min}$</td>
<td>Distance of closest interatomic approach</td>
</tr>
<tr>
<td>$r_e$</td>
<td>Evaporation rate</td>
</tr>
<tr>
<td>$r_s$</td>
<td>Distance from midpoint of substrate</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant (8.314 J/(mol K))</td>
</tr>
<tr>
<td>$R_e$</td>
<td>Electron range</td>
</tr>
<tr>
<td>$R_s$</td>
<td>Specific gas constant</td>
</tr>
<tr>
<td>$s$</td>
<td>Direction vector</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$T$</td>
<td>Absolute temperature</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Carrier gas temperature</td>
</tr>
<tr>
<td>$T_d$</td>
<td>Downstream temperature</td>
</tr>
<tr>
<td>$T_o$</td>
<td>Upstream temperature</td>
</tr>
<tr>
<td>$T_v$</td>
<td>Absolute temperature of an evaporant</td>
</tr>
<tr>
<td>$u$</td>
<td>Speed in first coordinate direction</td>
</tr>
<tr>
<td>$\bar{u}$</td>
<td>Average speed in first coordinate direction</td>
</tr>
<tr>
<td>$u_i$</td>
<td>Velocity</td>
</tr>
<tr>
<td>$U$</td>
<td>Speed of carrier gas stream</td>
</tr>
<tr>
<td>$U_{ll}$</td>
<td>Carrier gas velocity parallel to primary flow</td>
</tr>
<tr>
<td>$U_{\perp}$</td>
<td>Carrier gas velocity perpendicular to primary flow</td>
</tr>
<tr>
<td>$U_c$</td>
<td>Velocity of carrier gas stream</td>
</tr>
<tr>
<td>$U_{ccm}$</td>
<td>Velocity of carrier gas atom in center-of-mass system prior to collision</td>
</tr>
<tr>
<td>$U_v$</td>
<td>Velocity of vapor atom</td>
</tr>
<tr>
<td>$U_{vcm}$</td>
<td>Velocity of vapor atom in center-of-mass system prior to collision</td>
</tr>
<tr>
<td>$U_{pipe}$</td>
<td>Speed of carrier gas through inlet flow tube</td>
</tr>
<tr>
<td>$U_{pipe}$</td>
<td>Pumping capacity</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>$\dot{U}_{pump}$</td>
<td>Pumping capacity</td>
</tr>
<tr>
<td>$v$</td>
<td>Speed in second coordinate direction</td>
</tr>
<tr>
<td>$\bar{v}$</td>
<td>Average speed in second coordinate direction</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume</td>
</tr>
<tr>
<td>$\dot{V}$</td>
<td>Molar density of material</td>
</tr>
<tr>
<td>$V(r)$</td>
<td>Interatomic potential</td>
</tr>
<tr>
<td>$w$</td>
<td>Speed in third coordinate direction</td>
</tr>
<tr>
<td>$\bar{w}$</td>
<td>Average speed in third coordinate direction</td>
</tr>
<tr>
<td>$W$</td>
<td>Molecular weight of an evaporant</td>
</tr>
<tr>
<td>$W$</td>
<td>Power</td>
</tr>
<tr>
<td>$x$</td>
<td>Collision</td>
</tr>
<tr>
<td>$x$</td>
<td>Position</td>
</tr>
<tr>
<td>$x_m$</td>
<td>Mach disk distance from nozzle exit</td>
</tr>
<tr>
<td>$z$</td>
<td>Third coordinate axis</td>
</tr>
<tr>
<td>$Z_A$</td>
<td>Atomic number of carrier gas</td>
</tr>
<tr>
<td>$Z_B$</td>
<td>Atomic number of vapor atom</td>
</tr>
<tr>
<td>$Z_{\text{Cu}_2}\text{-He}$</td>
<td>Volume collision frequency</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Center of mass scattering angle</td>
</tr>
<tr>
<td>$\chi_{\text{cutoff}}$</td>
<td>Minimum angle used during scattering calculations</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Efficiency of energy utilization</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Ratio of specific heats ($c_p/c_v$)</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Mean free path</td>
</tr>
<tr>
<td>$\lambda_e$</td>
<td>Effective mean free path</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Angle</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Magnitude of normal distribution for specific value of $U_c$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
</tr>
<tr>
<td>$\rho_o$</td>
<td>Settling chamber gas density</td>
</tr>
<tr>
<td>$\sigma_{ji}$</td>
<td>Viscous stress tensor</td>
</tr>
<tr>
<td>$\sigma(\chi)$</td>
<td>Angular differential cross-section</td>
</tr>
</tbody>
</table>
### List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{aCu}$</td>
<td>Activity radius of a copper atom</td>
</tr>
<tr>
<td>$\sigma_{aCu2}$</td>
<td>Activity radius of an unstable dimer</td>
</tr>
<tr>
<td>$\sigma_d$</td>
<td>Directed momentum transfer cross-section</td>
</tr>
<tr>
<td>$\sigma_{rCu}$</td>
<td>Hard sphere radius of a copper atom</td>
</tr>
<tr>
<td>$\sigma_{rCu}$</td>
<td>Hard sphere radius of a helium atom</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Time of flight</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Reduced mass of a collision event</td>
</tr>
<tr>
<td>$\mu/\rho$</td>
<td>Mass absorption coefficient</td>
</tr>
<tr>
<td>$\xi$</td>
<td>Standard deviation</td>
</tr>
</tbody>
</table>
# Table of Contents

## Introduction

1. **Vapor Phase Synthesis of Materials**
   - Page 1
2. **Applications Motivating Vapor Phase Process Development**
   - Page 3
3. **Goals of the Dissertation**
   - Page 6

## Background

1. **Vapor Creation Using an Electron Beam Gun**
   - Page 10
   1. **Pure metal / metal alloy processing**
   - Page 12
   2. **Compound processing**
   - Page 16
   3. **Vacuum regime**
   - Page 17
2. **Vapor Transport**
   - Page 20
   1. **High vacuum vapor transport**
   - Page 21
     1. **Spatial distribution**
     2. **Angular distribution**
     3. **Kinetic energy**
     4. **Deposition efficiency**
   2. **Modification of vapor transport characteristics**
   - Page 26
     1. **Spatial distribution**
     2. **Angular distribution**
     3. **Kinetic energy**
     4. **Deposition efficiency**
     5. **Evaporated material form**
   3. **Jet Vapor Deposition™**
   - Page 34
   4. **Supersonic gas jet structure**
   - Page 37
   5. **Vapor transport modeling**
   - Page 39
3. **Vapor Adsorption and Diffusion on a Substrate**
   - Page 46
4. **Summary**
   - Page 49

## Invention of Directed Vapor Deposition

## DVD System Design

1. **Electron Beam Gun**
   - Page 50
   1. Maximum e-beam gun power requirements
   - Page 57
   2. Accelerating voltage selection
   - Page 60
   3. Selection of an e-beam generation source
   - Page 63
   4. A modified e-beam deflection system was required
   - Page 65
   5. Final e-beam gun configuration
   - Page 68
2. **Processing Chamber**
   - Page 69
Table of Contents

4.2.1. X-ray shielding for system user protection ........................................... 70
4.2.2. The chamber could accommodate various sources and substrates ....... 72
4.3 Crucible ........................................................................................................ 74
4.4 Gas System ...................................................................................................... 76
4.5 Vacuum Pumps .............................................................................................. 81
4.6 Vacuum Gauges ............................................................................................ 82
4.7 Substrate Temperature Control System ......................................................... 83
4.8 Computer Control Methodology ................................................................... 84
4.9 Concluding Remark ....................................................................................... 88

Experimental Investigation of Vapor Transport 90

5.1 Overview ........................................................................................................ 90
5.2 Accessible Processing Regime ........................................................................ 91
5.3 Visual Observations of Gas Stream ............................................................... 97
5.4 Gas Flow / Vapor Stream / Substrate Interactions ......................................... 102
  5.4.1. Carrier gas flux .......................................................... 103
  5.4.2. Mach number ............................................................ 106
  5.4.3. Carrier gas type / e-beam power .................................. 109
  5.4.4. Carrier gas flux / vapor stream interaction with substrate / crucible . 112
5.5 Concluding Remarks ..................................................................................... 115

Materials Synthesis Via Directed Vapor Deposition 116

6.1 Overview ....................................................................................................... 116
6.2 Contamination Study of Nonreactive Deposition ............................................ 117
6.3 Study of Silicon Deposition .......................................................................... 119
6.4 Study of Reactive Deposition ....................................................................... 126
6.5 Concluding Remarks .................................................................................... 128

Experimental Investigations of Deposition Efficiency 129

7.1 Overview ....................................................................................................... 129
7.2 Deposition Efficiency Experimental Procedures ............................................. 131
7.3 Flat Substrate Results ................................................................................... 132
  7.3.1. Carrier gas flux / Mach number ........................................ 133
  7.3.1.1 Vapor transport visualizations help explain efficiency results
  7.3.1.2 A discussion of evaporation rate variations
  7.3.1.3 Deposited film appearance, adhesion depend on process conditions
  7.3.1.4 A summary of initial deposition efficiency results
  7.3.2. E-beam power (evaporation rate effects) .......................................... 142
  7.3.2.1 Low beam power experiments generate inconsistent results
  7.3.2.2 Visual inspection of films revealed chamber pressure and beam power effects
7.3.2.3 A summary of evaporation rate results
7.3.3. Crucible to nozzle separation effects ........................................ 147
    7.3.3.1 Initial vapor distribution effects upon deposition efficiency
    7.3.3.2 Summary of nozzle position experiments
7.4 Fiber Substrates ................................................................................... 151
    7.4.1. Fiber coating deposition efficiency trends mirror flat substrate results 152
    7.4.2. Non line-of-sight deposition enhances deposition efficiency .......... 155
    7.4.3. Inspection of coated fiber characteristics ................................. 155
    7.4.4. Summary of fiber coating study .......................................... 157
7.5 Clustering ............................................................................................ 158
    7.5.1. Clustering probabilities for various process conditions .......... 160
    7.5.2. Ionization effects upon cluster formation probability ........... 163
7.6 Summary ............................................................................................. 164

Vapor Transport Model Development 166
8.1 Direct Simulation Monte Carlo (DSMC) Modeling of the Flowfield ...... 168
    8.1.1. Selection of discrete atom modeling method .......................... 168
    8.1.2. Adaptation of DSMC code to DVD .................................... 170
8.2 Biatomic Collision Theory (BCT) Modeling of Vapor Transport ......... 177
    8.2.1. Initial conditions ......................................................... 178
    8.2.2. Distance between collisions ........................................... 181
    8.2.3. Calculation of the directed momentum transfer cross-section ($\sigma_d$) 183
    8.2.4. Determination of the range of atomic interaction ($b_{\text{max}}$) .... 186
    8.2.5. Collision event ....................................................... 191
8.3 Summary ............................................................................................. 196

Vapor Transport Model Verification 198
9.1 Verification of DSMC Results ............................................................. 198
9.2 BCT Model Verification ................................................................. 200
    9.2.1. Random walk ........................................................... 201
    9.2.2. Atomic energy loss .................................................... 205
9.3 Summary ............................................................................................. 211

Vapor Transport Modeling of DVD 212
10.1 Vapor Transport Predictions ............................................................ 213
    10.1.1. Model predicts redirection at lower pressures than experiments ... 216
    10.1.2. Dissipation of jet’s fast flow limits vapor direction to substrate ... 217
    10.1.3. Adatom kinetic energies are below initial evaporation energies ... 218
    10.1.4. Adatom angle of incidence determined by gas near the substrate ... 220
    10.1.5. Flowfield temperature and pressure ..................................... 221
10.2 Vapor Deposition Predictions ......................................................... 223
10.2.1. Model predicted deposition efficiency trends ......................... 223
10.2.2. Vapor concentration effects ..................................................... 226
10.2.3. Predicted efficiencies ................................................................. 226
10.2.4. Deposition energy distributions change little with process conditions 227
10.2.5. Deposition angle distributions .................................................. 228
10.2.6. Deposition distribution ............................................................... 229

10.3 Summary ..........................................................................................231

**DVD System Development** .................................................................234

11.1 Reconfiguration of the Gun, Vapor Source, and Carrier Gas Flow ..........235
  11.1.1. Justification for system reconfiguration ........................................ 235
  11.1.2. Model-based analysis of system reconfiguration ............................ 237
11.2 Substrate Bias ..................................................................................242
11.3 Experimental Work ...........................................................................243
11.4 Model Development .........................................................................245
11.5 Concluding Remarks ........................................................................248

**Discussion** .........................................................................................249

12.1 Focus, Efficiency, and Angular Distribution .................................... 250
12.2 Non-line-of-sight Coating ................................................................. 251
12.3 Vapor Stream Mixing ........................................................................253
12.4 Enhanced Energy Deposition ............................................................. 253
12.5 Rapid, Continuous Processing of Pure Materials and Compounds .........255
12.6 Other Applications ............................................................................256
12.7 Other System Configurations ............................................................257
12.8 Summary ..........................................................................................257

**Conclusions** .......................................................................................258

13.1 Specific Conclusions ..........................................................................259
13.2 Final Thought .....................................................................................262

**References** ..........................................................................................263

**Appendix A - DVD Specifications** ......................................................276

  A.1 E-beam Gun Design Drawings ......................................................... 276
  A.2 Processing Chamber Design Drawings ............................................ 281
  A.3 Water-Cooled Crucible Design Drawings ....................................... 282
  A.4 Processing Chamber Pumping Capacity Design Calculations ............. 283

**Appendix B - Clustering Calculations** ................................................286

**Appendix C - Flowfield Modeling Code** ...........................................287
Appendix D - Atom Tracking Code 329
Appendix E - E-beam Vapor Distribution 348
Chapter 1

Introduction

1.1 Vapor Phase Synthesis of Materials

Since Grove observed metal deposits sputtered from a glow discharge in 1852 [1] and Faraday experimented with metal wire explosion in an inert atmosphere five years later [2], researchers have synthesized a multitude of materials from the vapor phase, sought to understand the properties of those materials, and explored their scientific and technological applications. Film property research was limited until the 1940’s when vacuum technology improvements allowed clean films to be created with reproducible properties. Since then, engineers have realized that vapor phase created materials (i.e. materials created via physical vapor deposition (PVD) or chemical vapor deposition (CVD)) can meet the design requirements of countless products. In some cases a thin film meets the engineering need (e.g. an environmental [3] or wear resistant [4] coating). In other cases vapor phase processing represents the only method by which the desired material can be applied (e.g. optical gold coatings for lenses, mirrors, and cathode ray tubes [3] or aluminum and copper metallization layers which interconnect semiconductor devices [5]). In still other instances vapor phase synthesized films have unique properties and microstructures not
found in bulk processed materials (e.g. giant magnetoresistive (GMR) multilayers [6], thermal barrier coatings (TBC) [7], and functionally graded materials (FGM) [8, 9, 10]).

Since the 1940’s researchers have developed vapor creation methods to synthesize thin film materials (e.g. electron beam evaporation [11], diode and magnetron sputtering [12], CVD [12], reactive evaporation (RE)\(^1\) and activated reactive evaporation (ARE)\(^2\) [13, 14, 15], ion plating [16, 17], and ion-beam assisted deposition [18]). Even as these and other technologies are increasingly employed in manufacturing systems, new material demands press the scientific limits of vapor phase processing ability. Engineers and scientists repeatedly confront obstacles which hamper the attainment of processing goals. These obstacles include the high cost of vapor deposition, the material utilization efficiency limits associated with line-of-sight high vacuum coating, the difficulty of controlling deposit composition in thermal evaporation systems, and the slow material creation rates of sputtering systems. To overcome these and other processing hurdles, materials engineers reinvestigate material synthesis methods and search for new avenues to vapor phase material creation as they seek to uncover techniques affording greater processing capabilities (e.g., deposition of precise material compositions with unique microstructures).

Indeed, despite the impressive sophistication of today’s vapor phase processing, there appear to be numerous unexplored variations of the vapor phase materials synthesis techniques in use which could help create new products that depend upon their material properties for success. An historical perspective highlights the short length of time that vapor phase processing has had to evolve and suggests that with further exploration, vapor deposition technology can evolve to currently inconceivable levels of sophistication (Fig. 1.1).

---

\(^1\) reactive evaporation - evaporation in presence of a low partial pressure of reactive gas (e.g. oxygen or hydrogen).

\(^2\) activated reactive evaporation-similar to reactive evaporation except that one or more reactants is activated, i.e. ionized to form a plasma. This increases system reactivity.
Chapter 1. Introduction

1.2 Applications Motivating Vapor Phase Process Development

Two specific industries demanding enhanced physical vapor deposition (PVD) process technology are the aerospace and semiconductor device industries. Fig. 1.2 shows several products from these fields which engineers would like to produce using vapor phase synthesis techniques:

- Oxidation resistant bond coats and ceramic insulating layers onto turbine blades.
- Adhesion layers and via filling materials for semiconductor interconnects.
- SiO₂, polysilicon, and aluminum layers for thin film transistors.
- Oxides, alloys, and pure metals which comprise laminated multilayers.
- Metal and intermetallic alloys which envelope fibers used in continuous fiber reinforced composites.

Figure 1.1 Evolution of Materials Processing. This timeline illustrates how little historical time has been spent developing vapor phase processing compared to solid or liquid phase material synthesis. (Figure courtesy of D.M. Elzey.)
While innovative new PVD techniques could contribute to the synthesis of more products than those shown, this short list suggests the breadth of utility for new vapor phase film synthesis technology in these industries. Short descriptions of these industries’ needs provide further evidence of the motivation for enhanced vapor phase material synthesis.

The aerospace industry wants to use metal matrix composites (MMC’s) in higher temperature propulsion systems to increase aircraft speeds and engine power output [19, 20]. To make MMC’s economically competitive, industry experts estimate that tens of thousands of pounds of coated continuous ceramic fiber reinforcement must be produced yearly at a per pound cost comparable to that of current single crystal, superalloy turbine blades [21].

**Figure 1.2** Engineering materials via PVD. The potential applications for enhanced PVD technologies are numerous.
The MMC’s produced from these coated fibers must also be microstructurally suitable for subsequent process steps (e.g. hot isostatic pressing) [20] and without fiber / matrix interface degradation due to excessive processing-induced stresses [22, 23] or reaction zone growth [24]. Storer [21] has indicated that current evaporation, sputtering, and CVD systems could lack the ability to create these advanced materials rapidly and economically enough to make continuous fiber reinforced MMC use a viable alternative. However, Storer has suggested that a high rate (> 10 \( \mu \text{m/min} \)), non-line-of-sight coating system could be economically viable [21].

Not only does the aerospace industry need an economic synthesis pathway for fabricating engine components such as compressor blades, blings (Rolls Royce), and fan frames (GE Aircraft Engines / Pratt & Whitney) [25, 26] but also it would like to apply a thermal barrier coating (TBC) to turbine blades used in engine hot sections. These TBC’s prevent blade oxidation at the high operating temperatures encountered and insulate the blades from the hot gas temperatures in the engine [7]. Many of the coatings envisioned for this application consist of highly engineered microstructures which require significant processing flexibility for their manufacture (e.g. composition and microstructure control). For these TBC’s, materials engineers want to produce porous microstructures of refractory (high melting point) metals and compounds [27, 28]. If a new PVD process can deposit material efficiently at different adatom energies, angles, and deposition rates, it may provide unparalleled process flexibility for the generation of useful, well-adhered, porous coatings.

In the semiconductor industry, the needs are different but equally demanding. For instance, dense metallic films often must be deposited onto engineered semiconductor devices containing precise doping concentrations in exact locations. Excessive substrate heating during processing can destroy the device by providing energy for implant diffu-
sion or for alloying between previously deposited metallization layers [5]. Studies suggest that use of a process which increases adatom kinetic energy could produce quality microstructures at reduced substrate temperatures [29 - 33].

In another electronic application, the ability to form polysilicon on a glass substrate maintained at a temperature below 600°C could replace the slow, expensive two-step deposit and anneal process currently used to produce thin film transistors [34]. Again, enhancement of adatom kinetic energy could hold the key to achieving this process capability.

An equally challenging manufacturing issue for the semiconductor industry is the filling of the small openings in the surface of a device “that connect the interconnect ‘wiring’ with the source, drain, and gate of the CMOS\(^1\) transistor, and those that connect one level of wiring with the underlying or overlaying level” [35]. As semiconductor designers make their devices smaller and smaller, the depth to width ratio of the device’s metal interconnect vias increases, from 1:1 in the 1980’s to 4:1 in the late 1990’s. As this ratio increases, the difficulty of filling these trenches completely with the desired metal also increases. The most technologically valuable via filling process of the late 1990’s and early 21st century will be able to fill these trenches with copper and other metal or metal compounds by means of line and non-line-of-sight techniques [35, 36].

### 1.3 Goals of the Dissertation

This dissertation’s work represents the first steps in the process of invention, discovery, and development of a new physical vapor deposition technology, termed Directed Vapor Deposition (DVD). This DVD technology has been envisioned most particularly as a method for depositing pure refractory (i.e. high melting point) elements, compounds, and

\(^1\) CMOS - complementary metal-oxide semiconductor
alloys rapidly and efficiently onto complex shapes. It is hoped that this research of PVD technology will lead to the introduction of a viable approach to vapor deposition into the mainstream of industrial vapor phase materials synthesis, particularly to meet the needs of the aerospace industry as it seeks to introduce continuous fiber reinforced (CFR) MMC’s into wide scale use. The work presented in this dissertation should allow many of the capabilities of this technology to be assessed for refractory material and also for other vapor phase material system applications such as those important to the semiconductor industry.

The next chapter of this dissertation reviews today’s state-of-the-art in vapor phase processing of refractory elements, compounds, and alloys. The analysis identifies reasons why it should be possible to enhance current refractory material PVD technology, in particular electron beam (e-beam) evaporation. Specifically, Chapter 2 will examine ways to modify standard e-beam system operating conditions to achieve enhanced refractory material processing. The invention of such a modified e-beam based PVD system is then described in Chapter 3. The design and reduction to practice of this new technology are presented in Chapter 4.

Chapter 5 experimentally investigates vapor transport in the Directed Vapor Deposition environment and seeks to develop an understanding of the effect of the system’s unique vapor transport means upon the vapor stream’s inherent characteristics. The work reported in Chapters 6 and 7 demonstrates the material processing capability of DVD by experimentally investigating the system’s ability to create films with low contamination levels, to synthesize amorphous and polycrystalline silicon on glass substrates, to create zirconia coatings via reactive deposition, and to deposit material efficiently onto flat and fibrous substrates. Chapters 6 and 7 generate numerous results which allow the vapor phase material synthesis utility of the technique to be assessed.
Chapter 8 uncovers modeling methodologies applicable to vapor transport in DVD and other similar technologies and uses those techniques to develop a model of interaction between evaporated atoms, background gas atoms in the chamber and the substrate. After model verification in Chapter 9, Chapter 10 uses the model to provide additional insight into the experimental deposition efficiency results and into the system’s general material synthesis behavior. In Chapter 11 the dissertation’s model is used to suggest a different system configuration which may facilitate more efficient materials synthesis for various vapor phase coating applications.

While the DVD system developed in this research may or may not become a pathway for the economic creation of tomorrow’s aerospace and electronic products, the knowledge generated through its study should contribute to the understanding of physical vapor deposition. Chapter 12 uses the results of the preceding chapters to assess the potential advantages of DVD, to identify those which appear to be attainable, and to suggest which material synthesis problems DVD might be well suited to attack. The overall organization of the dissertation is summarized in Fig. 1.3.
Figure 1.3  **Dissertation organization.** This dissertation contributes to science through development of new PVD technology, experimental and modeling analysis of that technology, and identification of its material synthesis utility.
Chapter 2

Background

As noted in section 1.3 of the previous chapter, the core motivation for this dissertation’s research has been a desire to discover an improved method for the deposition of refractory elements, compounds, and alloys rapidly, efficiently, and with little contamination. As the previous chapter also noted, Storer [21] has suggested that an economically feasible method for depositing such film structures onto complex shapes could be some type of non-line-of-sight coating technique. When attempting to identify a vapor deposition method which meets all of these requirements, the desired process capabilities do not appear to be available in one existing technology.

Sputtering deposits material slowly (~1 µm/min [12] versus 1 mm/min for e-beam systems [11]). Sputtering rates are generally low due to the difficulty of sustaining the intense plasma discharge density necessary for higher rate deposition [12]. Standard e-beam technology generates low deposition efficiencies (only line-of-sight deposition) when coating small cross-section substrates like continuous fibers to be used in metal matrix composites. Non-line-of-sight coating does not occur in e-beam systems because evaporation in these systems almost always occurs in high vacuum (pressures less than $10^{-1}$ Pa / $10^{-3}$...
Torr)\(^1\) where material transfer occurs by collisionless, line-of-sight atomistic transport [11]. Resistive flash evaporators generally evaporate refractory materials slowly [12], and in these systems there is a risk of vapor stream contamination. Contact between a refractory evaporant source material (e.g. molybdenum) and an equally high melting point resistive heating target (e.g. tungsten) has a high probability of introducing both source material and heating target into the vapor stream. The apparent inability of any of these techniques to combine all of the desired processing abilities described in Chapter 1 has motivated thought about previously unconsidered material synthesis pathways.

This chapter examines the possibilities of modifying the desirable high rate electron beam evaporation tool so that it can perform uncontaminated line and non-line-of-sight material synthesis as efficiently as possible. In general, the process of vapor phase material synthesis consists of five steps:

1. Vapor creation.
2. Vapor transport.
3. Vapor adsorption onto the substrate.
5. Adatom movement by bulk diffusion through the growing film lattice to final positions.

Within the framework of these five steps, this chapter reviews the state-of-the-art of electron beam material synthesis and assesses its presently understood ability to synthesize engineering materials from the vapor phase.

\(^1\) 133.3 Pa = 1 Torr, 1 atmosphere = 760 Torr = 101,300 Pa, space vacuum = 10^{-12} Torr
This examination of vapor phase material synthesis is generally limited to e-beam processing due to the complexity of the physical processes involved in producing vapor with an e-beam and due to the distinctly different manner in which other, less desirable, PVD techniques like sputtering produce their vapor (i.e. less desirable for the specific applications focussed upon in this research). This chapter examines current experimental and theoretical understanding of how to enhance an e-beam system’s vapor atom deposition distribution, efficiency, angle, energy, and form (monatomic or cluster). Finally, a brief examination of known relationships between processing parameters and final film microstructures at the end of this chapter illustrates why, if a new system can be invented, a uniquely configured e-beam system could provide vapor phase material processing engineers with an ability to synthesize unique engineering products by changing vapor transport, and thus vapor deposition, characteristics from those of a conventional e-beam PVD system.

2.1 Vapor Creation Using an Electron Beam Gun

When reliable vacuum pumping technology in the 1940’s first made it possible to achieve vacuums at or below the milliTorr range (~0.10 Pa), scientists made use of the resulting long electron mean free paths to generate electron beams that evaporated elements, alloys, and compounds for engineering material synthesis. Use of e-beams has been extensive over the ensuing years in part because of their ability to evaporate and deposit a large variety of materials rapidly, cleanly, and with a minimum consumption of energy [11].

2.1.1. Pure metal / metal alloy processing

E-beam systems have demonstrated an ability to evaporate and deposit not only easy to process pure elements like aluminum, zinc, gold, and silver but also more difficult to pro-
cess low vapor pressure elements like molybdenum, tungsten, and carbon, and highly reactive elements such as niobium, titanium, and tantalum [37]. E-beam systems evaporate and deposit all of these elements by cleanly bringing the heat source (electrons) directly into contact with the source material, often contained as a “skull” melt inside a water-cooled crucible (Fig. 2.1). A crucible is frequently used to contain the source material because it maintains solid source material (a “skull”) between the crucible wall and the molten evaporant pool, preventing vapor source contamination from the crucible.

Researchers have also demonstrated that alloys with a vapor pressure ratio as high as 1000:1 between their elements can be e-beam evaporated from a single crucible source and deposited with the correct chemical composition [38, 39]. This ability is crucial to the fabrication of materials for the MMC aerospace application described in Chapter 1 (e.g. deposition of Ti_xMo_{1-x}, (Ti_2Al)_xNb_{1-x}, or Ti-6wt%Al-4wt%V) [20, 21, 38, 39]. For alloys with elements having a greater vapor pressure ratio, lower melting point (and higher activity) material can be wire fed into a pool of the more refractory material [20] or separate element evaporation from adjacent crucible sources can be employed [11, 37]. When separate crucible evaporation is employed, alloys are created by mixing atomic fluxes as shown in Fig. 2.1.

E-beam processing of pure elements and alloys does present challenges to those attempting to control deposition characteristics precisely. During single crucible alloy processing, the initial vapor stream is rich in the more volatile component(s) of the feed-stock due to differences in evaporation rate for elements in the alloy. Langmuir [11] has provided a general relationship between an element’s evaporation rate, given as a mass flux, and its molecular weight, vapor pressure, and temperature:

\[ a \propto P_s \left( \frac{W}{T_v} \right)^{1/2} \]  

(2.1)
Chapter 2. Background

where

\[ a = \text{Specific evaporation rate (kg/(m}^2 \text{ sec))}, \]

\[ P_s = \text{Saturated vapor pressure at a temperature } T_v (\text{Pa}) [2], \]

\[ W = \text{Molecular weight of the evaporant (kg/mol), and} \]

\[ T_v = \text{Absolute temperature of the evaporant (K)}. \]

Figure 2.1 **Multicrucible e-beam deposition.** Material in region (AB) can create an alloy that is approximately of the correct composition if the substrate is translated.

Not only do elements initially leave the crucible at different rates due to differences in vapor pressure but also, for some length of time thereafter, the compositions of the melt pool and vapor stream continue to change until the compositions of the solid rod stock and the molten pool reach a stable equilibrium (i.e. until the rate at which vapor constituents A and B leave the molten pool equals the rate at which they are introduced from the solid) [11, 12]. Reaching this equilibrium state adds significantly to the processing cycle time.
(potentially hours), wastes valuable source material, and decreases system flexibility [11, 40]. While multiple crucible evaporation can sidestep this time dependent composition fluctuation, alloy processing from multiple crucibles in a high-vacuum e-beam system creates a stoichiometrically correct deposit only in that region above the crucibles where the vapor clouds of the neighboring crucibles intersect [11]. As a result, significant amounts of expensive vapor can be wasted (Fig. 2.1). Even in this region, small compositional differences exist as a result of variation in the vapor density distribution from the e-beam source and vapor collisions between species A and B which lead to different rates of interdiffusion [11]. Substrate translation is usually employed to reduce compositional gradations across the film surface.

In addition to vapor flux composition distributions which vary with time or position, all e-beam systems exhibit a vapor spatial density distribution which is nonuniform and dependent upon numerous process variables [39, 41]. It has been reported throughout the literature that atoms ejected from an e-beam target take on a distribution described by [12]:

\[ I(\theta) = I_o \cos^n\theta \]  

(2.2)

where \( I(\theta) \) = Vapor stream density in a direction \( \theta \) degrees from the normal to the vapor emitting surface,

\[ I_o = \text{Vapor stream density for } \theta = 0, \text{ and} \]

\[ n = 2, 3, 4, \text{ or more.} \]

While the vapor stream emerging from a planar surface element takes on a \( \cos \theta \) distribution (where \( n = 1 \)) [2], numerous authors note that e-beam vapor streams rarely exhibit this simple cosine vapor distribution for various reasons as described in Fig. 2.2 [11, 2, 42]. In addition to the influences shown in Fig. 2.2, e-beam vapor stream distributions also
depend upon the e-beam scanning cycle employed (rate and pattern) and the specific material evaporated [11, 38].

![Diagram of vapor distribution in an e-beam system]

**Figure 2.2  Vapor distribution in an e-beam system.** Several factors can combine to modify an e-beam evaporator’s vapor flux distribution [11].

### 2.1.2. Compound processing

In addition to an ability to deposit pure elements and alloys, e-beam systems have demonstrated a reasonable ability to create material from compound sources. For compounds which are poor conductors of electricity and heat, some combination of reduced e-beam
power densities (below 2x10⁷ W/m²) [1], specialized e-beam scan patterns [1], and partially dense source materials (e.g. 60% dense yttria-stabilized zirconia for TBC applications [43]) are usually necessary to prevent source material cracking and generate a controlled vapor stream. When working with complex compound source materials like yttria-stabilized zirconia, vapor pressure problems can arise that are similar to those described for single crucible alloy evaporation.

A more common problem during compound evaporation is dissociation of the constituent elements, an event which precludes stoichiometrically correct film creation unless the lost elements are replaced during deposition [11]. While some compounds exhibit minimal dissociation with little of the gaseous element being removed by the process chamber vacuum pump [11, 15], most require introduction of additional reactive gas into the work chamber for useful RE or ARE deposition [2, 11, 15, 37, 44, 45]. RE allows compounds to reform during deposition by introducing reactive species into the processing chamber and raising the chamber pressure as high as 1 Pa (~10⁻² Torr). A primary drawback of RE for dense film synthesis is vapor atom thermalization¹ leading to film porosity due to reduced adatom kinetic energy [11, 15]. Vapor atom thermalization during reactive evaporation has motivated development of ARE in which plasma-enhanced reactivity of the gas environment makes possible a decrease in reactive gas pressure, a corresponding reduction in gas/vapor collisions, and a minimization of vapor atom thermalization [11, 15].

2.1.3. Vacuum regime

E-beam material synthesis has occurred almost exclusively in chamber pressures below 10 Pa (~10⁻¹ Torr). However, recent material processing efforts by Eastman, Halpern, and

¹ thermalization- a change in the velocity and energy of an atom towards the average velocity and energy of the surrounding gas as the result of momentum transferring atomic collisions.
others [46, 47] have demonstrated that useful vapor phase materials can be created at higher chamber pressures. Eastman et al. have used e-beam evaporation to create nanophase $\gamma$-Al$_2$O$_3$ clusters with a mean grain size of 2.5 nm in a 1 Torr (~$10^{-2}$ Pa) oxygen rich environment while Halpern et al. have deposited resistively-evaporated gold by transporting vapor to a substrate in a helium gas jet at chamber pressures around 1 Torr.

Despite the work of Eastman and the development of RE and ARE processes for compound production which have utilized e-beam systems with chamber pressures up to 1 Pa (~$10^{-2}$ Torr), many researchers believe that e-beam film synthesis in reduced vacuum is not viable. This mindset has developed as a result of certain widely accepted “rules of e-beam processing.” The literature [11, 18, 37] generally states that e-beam vapor-phase processing must occur in high vacuum because:

- Operating an e-beam gun with pressures greater than $1x10^{-2}$ Pa (~$10^{-4}$ Torr) in the electron generating workspace can result in dielectric breakdown of the reduced vacuum environment and high voltage arcing (i.e. shorting) between the negatively charged filament and nearby portions of the gun maintained at different electrical potentials. Thus, energy for source evaporation is instead transferred to the gun, potentially damaging it and preventing low vacuum e-beam processing [11].

- The tungsten filaments which generate electrons in many e-beam evaporation systems degrade rapidly in low vacuum or atmospheric pressure. Thus, if the vacuum in the filament workspace is poor, electron emission from the filament generates ions which bombard and erode the filament, preventing low vacuum processing [48].

- If the entire system’s pressure exceeds $1x10^{-2}$ Pa, e-beam energy dissipation occurs via gas scattering in the gun and process chamber, and the energy is unavailable for material evaporation, making low vacuum e-beam processing unfeasible [11, 49].

- Conducting film synthesis in a low vacuum environment leads to vapor atom thermalization and poor quality deposit microstructures [11].
• Operating in high vacuum has often been considered necessary to avoid contamination [11, 50]. This belief has led to the development of long process cycles in which the chamber is evacuated below $10^{-2}$ Pa, the chamber and its internal fixtures are heated to “bake-out” contaminants prior to deposition, and deposition occurs at a pressure low enough to ensure few evaporant atoms react with contaminant particles. It has also produced processing rules stating that “for pure films a pressure/deposition rate ratio of $< 10^{-7}$ Torr/Å/sec [10^{-5} Pa/Å/sec] must be achieved” [51].

Although many researchers have deemed e-beam vapor phase material synthesis in reduced vacuum impractical [11, 12, 37], other researchers have demonstrated the feasibility of low vacuum / atmospheric e-beam material processing.

The need to weld thick steel plates for ships and submarines and a desire to use e-beams to induce chemical reactions has motivated research into methods of conducting e-beam material processing at pressures above $10^{-2}$ Pa, even in open atmosphere [11]. These applications have led to the development of e-beam guns employing either transparent thin foil windows or differentially pumped gun sections to decouple the high vacuum e-beam generating space from the low vacuum / atmospheric processing region [11, 52 - 56]. While 25 µm thick electron “transparent” windows of Ti or Al work in e-beam guns employing high accelerating voltages (i.e. > 30 kV) and low power densities, an open unimpeded path from filament to target is required for high current density welding systems [53]. During the 1960’s, systems with such electron pathways were perfected in which electrons could be generated in a $10^{-5}$ Pa workspace evacuated by one pump, passed through two separately pumped gun segments at $10^{-2}$ Pa and 1 Pa, and used to weld metal parts at atmospheric pressure. While these welders occasionally experienced filament erosion or high voltage breakdowns resulting from sudden pressure rises in the filament workspace (due to vapor bursts from the workpiece), they have demonstrated the feasibility of low vacuum / atmospheric material processing [11].
E-beam operation under reduced vacuum or atmospheric conditions has also been improved by maximizing beam propagation through the gas environment in the gun and processing chamber. Fundamental investigations of e-beam / gas interactions by Boedecker, et al., Arata, and others [11, 49, 57] have revealed that the most important factors affecting beam propagation are the beam path length through the increased pressure, the e-beam’s accelerating voltage, and the molecular weight of the gas through which the beam propagates. Thus, when processing material under low vacuum or atmospheric pressure, beam propagation can be maximized by passing the e-beam into the elevated pressure regime close to the target and by decreasing the scattering cross-section of the gas in the processing chamber (i.e. by using a high e-beam accelerating voltage and a low molecular weight gas in the processing chamber) [48, 49].

### 2.2 Vapor Transport

After atomistic vapor has been created with a PVD tool like an electron beam gun, vapor transport to the substrate occurs either as a result of the vapor creation process itself (e.g. thermal evaporation energy) or can be effected by various external means acting upon the individual vapor atoms (e.g. interaction with electric or magnetic fields or as the result of collisions with gas atoms in the chamber). Indeed, the particular method and process conditions used to generate the vapor stream have been shown to influence significantly the spatial distribution, angle of incidence, kinetic energy, deposition efficiency, and form (e.g. monatomic or multiatom clusters) of vapor atoms reaching a substrate. Process-induced modifications of these parameters critically affect film growth (section 2.3).
2.2.1. High vacuum vapor transport

Often, the inherent characteristics of a high vacuum e-beam vapor stream (e.g. deposition efficiency and spatial, angular, and energy distribution) do not coincide with the optimal vapor stream characteristics desired for an application.

2.2.1.1 Spatial distribution

As section 2.1.1. explained, the vapor distribution from an e-beam source can be described by equation (2.2) in which $n = 2, 3, 4$ or more. This diverging, nonuniform vapor distribution can cause material processing difficulties in some applications. For instance, when coating fibers, the vapor stream of e-beam systems (Fig. 2.3) leads to significant variation of the material deposition rate on neighboring fibers. The magnitude of this nonuniform coating (onto flat substrates) has been described using the following equation [11]:

$$\frac{d_s}{d_{so}} = \frac{1}{\left[ 1 + \left( \frac{r_s}{h_v} \right)^{2\left( n + 3 \right)/2} \right]}$$

(2.3)

where: $d_s = \text{Local film thickness on a flat substrate}$, $d_{so} = \text{Film thickness directly above vapor source}$, $r_s = \text{Distance from midpoint of substrate}$, $h_v = \text{Source to substrate separation distance}$, and $n = \text{Exponent as used in equation (2.2)}$.

In the fiber coating application, nonuniform vapor deposition is generally undesirable and could result in improper fiber spacing in a consolidated composite material (Fig. 1.2).
For all substrate surfaces, the diverging vapor streams of Figs. 2.1 - 2.3 lead to variation in the angle of vapor deposition with lateral position and with source-to-substrate separation. When coating large substrates with variable surface topologies (e.g., trenches and vias on 200 - 300 mm semiconductor wafers), this leads to an angular deposition which can prevent proper coating of non-line-of-sight surfaces [58].

2.2.1.2 Angular distribution

For all substrate surfaces, the diverging vapor streams of Figs. 2.1 - 2.3 lead to variation in the angle of vapor deposition with lateral position and with source-to-substrate separation. When coating large substrates with variable surface topologies (e.g., trenches and vias on 200 - 300 mm semiconductor wafers), this leads to an angular deposition which can prevent proper coating of non-line-of-sight surfaces [58].

2.2.1.3 Kinetic energy

During a thermal material synthesis process like e-beam evaporation, as energy is introduced into a liquid, some fraction of the atoms in the melt gain enough vibrational kinetic...
energy to overcome the intermolecular forces binding them to the liquid. Atoms leaving an e-beam melt generally have 0.1 - 0.2 eV of kinetic energy [59] and a tight energy distribution [60]. In the literature, the magnitude of the evaporation induced kinetic energy is generally related to the material’s vaporization temperature by the following Boltzmann temperature equation [11, 2, 61]:

$$E = \frac{3}{2} k T_v = \frac{1}{2} m v^2$$  \hspace{1cm} (2.4)

where \( E \) = Kinetic energy of the evaporated atoms (J), 
\( k \) = Boltzmann’s constant (1.381 x 10^{-23} J/K), and 
\( T_v \) = Vaporization temperature of the source (K).

Although it is not initially apparent why this relationship should be true, Maissel and Glang [2] have provided a semirigorous proof of equation (2.4). They explain that the speed \( c \) of any atom is comprised of three components \( u, v, \) and \( w \) perpendicular to each other. For an ensemble of atoms in a volume with different speeds, the mean square velocity of all \( N \) molecules is:

$$\frac{c^2}{u^2} = \frac{\sum u^2}{N}$$  \hspace{1cm} (2.5)

and the mean-square speed of those molecules is:

$$\frac{c^2}{u^2} = \frac{\sum c^2}{N} = u^2 + v^2 + w^2$$  \hspace{1cm} (2.6)
Kennard [62] and Parker [63] have demonstrated that, within a volume $V$, molecules with a mass $m$ and a velocity $u$ exert a pressure:

$$P = \frac{N}{V} m u^2$$  \hspace{1cm} (2.7)

on a flat surface perpendicular to the direction of $u$. If the velocities in different directions are assumed to be uniformly distributed, then:

$$u^2 = \frac{1}{3} c^2$$  \hspace{1cm} (2.8)

Substituting equation (2.7) into equation (2.8) yields:

$$P = \frac{N}{3V} m c^2$$  \hspace{1cm} (2.9)

Given the Universal Gas Law, an expression for the relationship between gas temperature and velocity can now be written:

$$\frac{1}{3} m c^2 = kT$$  \hspace{1cm} (2.10)

Multiplying equation (2.10) by $3/2$ gives an expression for kinetic energy and also equation (2.4).

More recently, Asano et al. [59] have demonstrated experimentally that actual atom velocities are frequently above the level suggested by the basic relation of equation (2.4). In a study of uranium, titanium, and copper mean atomic velocities, Asano et al. found that the mean velocity of each atom type exceeded the predicted thermal mean velocity. Uranium’s velocity was 2.1 times greater than predicted by equation (2.4) while titanium’s was 1.6 and copper’s 1.3. Interestingly, Asano et al. concluded that the increase in velocity was the result of electronic excited state energy to kinetic energy conversion during adiabatic
expansion away from the molten vapor source. (The exchange of excited state energy for kinetic energy has been demonstrated elsewhere during atomic collisions between alkali metals [64].) Asano et al. [59] explained that the increase in velocity was less substantial for copper due to its smaller number of possible excited states.

Whether the adatom energies in thermal evaporation systems are 0.2 eV or 1.3, 1.6, or 2.1 times that level, Thornton [65, 66, 67, 68] has experimentally demonstrated that substantially more energy per atom must be introduced into a growing vapor phase deposited material (> 0.5 eV) to generate dense microstructures at low substrate temperatures. Zhou et al. have used molecular dynamic modeling methods to illustrate this same requirement [31]. As section 2.2.2.3 will discuss, this energy requirement has led to the development of various methods of adatom energy enhancement so that useful films can be created for dense film applications.

2.2.1.4 Deposition efficiency

Frequently, applications require that vapor be deposited only in select locations (e.g., into the vias of semiconductor wafers and onto fibers for continuous fiber reinforced metal matrix composite creation). In their most basic configurations, high-vacuum e-beam (and sputtering) systems lack the ability to redirect their vapor stream after it leaves the source with a \( \cos^N\theta \) distribution. As a result, deposition into the deep trenches and vias which are a part of newer semiconductor devices is becoming increasingly difficult. Rossnagel et al. and Yang et al. have recently studied ways to tailor vapor stream angular distributions for the most efficient filling of electrical conduits on semiconductor devices [36, 54, 58, 69, 70]. The need to deposit materials efficiently in selected locations is also observed during line-of-sight fiber coating in high vacuum e-beam systems. Such systems often intersect little more than 5% of the total vapor stream (c.f. Fig. 2.3), allowing the rest of the highly refined, expensive matrix material to deposit uselessly onto the walls of the chamber.
2.2.2. Modification of vapor transport characteristics

Because the inherent characteristics of a high vacuum e-beam vapor stream sometimes do not generate desired material properties, researchers have developed ways to modify various aspects of the vapor stream [71].

2.2.2.1 Spatial distribution

Since the 1970’s, researchers have investigated ways to modify vapor distributions to produce a more uniform vapor stream and to enhance non-line-of-site coating. One of the more successful methods for varying the vapor stream distribution in e-beam systems has been to raise the background processing chamber pressure above $10^{-2}$ Pa ($\sim 10^{-4}$ Torr). Investigations by Beale and Grossklaus [44, 72] revealed that raising argon pressures to 0.1 Pa decreased the exponent for their $\cos^n\theta$ distribution from 8 to 5.5, indicating that higher chamber pressure led to a less focussed, more uniform coating. Interestingly, experimental investigations by Erikson et al. [73, 74] showed that, at argon pressures of $1 \times 10^{-4}$ Pa and higher, vapor focussing in their system became increasingly pronounced as chamber pressure rose (Fig. 2.4). While researchers generally agree that vapor distribution changes with varying gas pressure are the result of atomic collisions [11], the particular cause of vapor stream defocussing and then focussing with increasing chamber pressure has not been explained. In Erikson’s system, vapor atom clustering could have changed the effective mass of the vapor particles being scattered, decreasing their rate of lateral diffusion and increasing the focus of their final deposit. Alternatively, higher vapor pressures resulting from the elevated e-beam powers of Erikson’s study could have caused a more significant surface deformation of the source material and thereby generated a more focussed initial vapor stream (c.f. Fig. 2.2).
Another method investigated for vapor spatial density distribution variation has been substrate biasing. Erikson [73] reported that this did not change the distribution of vapor deposited from an ionized vapor cloud, and Krutenat [75] suggests that substrate biasing in combination with a plasma discharge between source and substrate led to “randomization” of the vapor stream and non-line-of-sight coating. The scattered depositions observed by Erikson and Krutenat are most probably the result of vapor/gas collisions between source and substrate with substrate biasing contributing little to vapor redirection. Although substrate biasing does not appear to affect vapor direction, Rossnagel et al. have shown that unbalanced magnetrons in sputtering systems are capable of affecting the distribution of vapor traveling from sputtering target to substrate [36, 54, 58, 70].

Figure 2.4 **Background gas pressure modifies vapor density distribution.** Results from Erikson’s study of medium vacuum e-beam deposition show an increase in vapor focus as argon chamber pressure is increased from 4 to 50 x 10⁻⁵ Pa. (Evaporation rate = 32 g/min. Source-to-substrate distance = 32.4 cm) [73]
2.2.2.2 Angular distribution

In sputtering systems, researchers have changed the angular distribution of vapor through the use of collimators and unbalanced magnetrons. Collimation [76] places a physical filter between source and substrate to allow passage of only the fraction of atoms traveling nearly normal to the substrate. While collimation facilitates microelectronic trench and via filling, it is slow and inefficient [76]. Use of an unbalanced magnetron, which forces charged sputtered particles to travel along electromagnetic field lines, has proven more useful as a means for efficiently modifying vapor distributions [58, 61]. In sputtering systems, Rossnagel and others [70] have successfully used electrostatic collimation to manipulate the ionized vapor flux angular distribution for more efficient trench filling.

2.2.2.3 Kinetic energy

In sputtering, cathodic arc, and certain RE/ARE e-beam systems negative bias voltages of 50 - 300 V are frequently applied to substrates to increase the energy of the incident charged species [12, 16, 18, 77]. Mattox [16] and others [78] realized in electron beam systems that interaction of the e-beam with the gas in the chamber created an ionized plasma of vapor atoms and chamber gas atoms. By applying a negative electrical bias (~100 V) to the deposition substrate, both ionized gas and vapor atoms could be accelerated towards the substrate as part of an “ion plating” process, imparting kinetic energies of 10-10,000 eV to depositing atoms [16]. Kinetic energies of this magnitude lead to significant film densification, the removal of some atoms deposited via sputtering, and the introduction of disorder into the growing film unless significant substrate heating is permitted.

2.2.2.4 Deposition efficiency

Limited studies have shown that PVD processing with moderate background chamber pressures can lead to significant non-line-of-sight deposition and, for certain system configurations, an increase in deposition efficiency [44, 79]. For flat substrate coating studies,
Bunshah and colleagues [44] reported an overall decrease in deposition efficiency with increasing chamber pressure, but, for substrates with surfaces not in the line-of-sight of the source, they noted that non-line-of-sight coating efficiencies could be enhanced by:

- Changing the mass of the scattering gas introduced into the chamber. Bunshah noted that, for a given chamber pressure, the amount of non-line-of-sight coating increases as the mass of the scattering gas molecule approaches that of the evaporant.

- Increasing the pressure of the scattering gas in the chamber. Introducing gas into the chamber increased non-line-of-sight coating, and higher chamber pressures resulted in more non-line-of-sight coating.

Bunshah and colleagues offered no physical insight into the root cause of these trends except to say that they were dictated by simple momentum exchange principles between gas and vapor atoms.

In a study of deposition onto fibrous substrates from a metal vapor laden Jet Vapor Deposition™ inert gas stream, Hill [79] noted than the mass capture efficiency of the fibers was greater than the cross-sectional area occupied by the fibers. Hill attempted to explain his observations using a continuum-based vapor diffusion model designed to predict lateral diffusion of vapor atoms across carrier gas streamlines. While Hill only explored copper deposition in a helium chamber pressure of 4 Torr, he suggested that the magnitude of non-line-of-sight coating could be varied with changes to the carrier gas stream velocity (i.e. Mach number). Highest deposition efficiencies were reached at Mach numbers of 1.0 - 1.2 with decreasing deposition efficiency at higher and lower Mach numbers.

### 2.2.2.5 Evaporated material form

Material processing in medium or high vacuum with e-beam systems most often generates individual atoms of material which deposit on various substrates to form a multitude of important film products [11, 12, 37, 61]. While atomistic vapor is the most common mate-
rial form desired by those employing e-beam systems, some researchers have demonstrated that slight modifications to the PVD environment can lead to the formation of significant numbers of vapor clusters (agglomerations of atoms) [46, 50, 79-89]. As noted in Fig. 2.2, extremely high evaporation rates in conventional e-beam systems can lead to the formation of a virtual vapor source above the source material surface. In this region the density of vapor atoms is high enough to lead to vapor / vapor atom collisions, redistributing the vapor stream and in some cases leading to vapor cluster formation [11]. The results of Erikson [73] (section 2.2.2.1) also emphasize the important effects of clustering upon the material creation characteristics of a vapor deposition system.

Even when vapor densities are not extremely high, vapor atom cluster formation has been reported to be common in low vacuum processing environments [90, 91], suggesting that the background chamber gas plays a role in cluster formation. As Steinwandel and Hoeschele explain [92], the cluster nucleation process occurs via a series of steps in which individual atoms (A) and some other atomistic or molecular species (M) collide:

\[
A + A + M \leftrightarrow A_2 + M^* \tag{2.11}
\]

\[
A_2 + A + M \leftrightarrow A_3 + M^* \tag{2.12}
\]

\[
A_{n-1} + A + M \leftrightarrow A_n + M^* \tag{2.13}
\]

After the collision event the third species often becomes energized by the collision event (M*). Steinwandel and Hoeschele point out that “The reaction sequence [equations (2.11) - (2.13)] is frequently formulated without the three-body collision partner \(M\). However, it should be noticed that three-body collisions are required due to the conservation laws of momentum, and energy for elementary reactions.” In the low vacuum environment, the third body will frequently be a background gas atom rather than a third vapor atom.
When attempting to describe cluster formation, numerous authors have taken a thermodynamic approach [86-88, 93-95] while others have pursued a kinetic activity explanation [96-100]. Study of the numerical results generated to date by both methods indicates that current kinetic models provide more reasonable predictions of experimental cluster formation results. Steinwandel and Hoeschele summarize [92]:

The classical [thermodynamic] theory of homogeneous nucleation is inadequate in order to describe the nucleation behavior of metal vapors at all degrees of supersaturation that could be realized experimentally. Nucleation appears to be a problem of elementary reaction kinetics in conjunction with a proper statistical thermodynamics formulation for stability criterions of small clusters.

The exact reaction kinetics and stability criterion appropriate to a particular system under study depend upon the characteristics of the system. For instance, as Smirnov and Strizhev note [100]: “The character of clustering is different for neutral and weakly ionized atomic beams. Ions of an atomic beam are nuclei of condensation, and the presence of charged atomic particles in an atomic beam is responsible for condensation of atoms.”

In a recent study of Jet Vapor Deposition™, a low vacuum vapor deposition technique, Hill [79] has calculated the probability of cluster formation for different processing conditions using a reaction kinetics approach and has used those results to delineate experimentally observed microstructures created during the coating of fibers. Hill calculated the importance of cluster formation by first determining the equilibrium concentration of unstable metal vapor dimer (i.e., prior to collision with a third body):

\[
[Cu_2^*] = \frac{[Cu]^2}{2} \frac{4}{3} \pi (\sigma_{aCu}^3 - \sigma_{rCu}^3)
\]

where \([Cu_2^*]\) = Concentration of unstable dimers (dimers/m^3),

\([Cu]\) = Concentration of metal monomer (atoms/m^3),
\[ \sigma_{aCu} = \text{Activity radius of a copper atom (m), and} \]

\[ \sigma_{rCu} = \text{Hard sphere radius of copper atom (m).} \]

Hill then indicated that the rate of stable dimer formation could be derived from:

\[ Z_{Cu_2-He} = [He][Cu_2\ast]\pi \left( \frac{\sigma_{aCu_2} + \sigma_{rHe}}{2} \right)^2 \left( \frac{8kT}{\pi \mu} \right)^{1/2} \] (2.15)

In which

\[ [He] = \text{Concentration of background gas (atoms/m}^3\text{),} \]

\[ \sigma_{aCu_2} = \text{Activity radius for the unstable dimer (m),} \]

\[ \sigma_{rHe} = \text{Hard sphere radius of a helium atom (m), and} \]

\[ \mu = \text{Reduced mass of collision, defined as} \frac{1}{\mu} = \frac{1}{\mu_{Cu}} + \frac{1}{\mu_{He}} \text{ (kg).} \]

Stable dimer formation then makes possible the formation of larger clusters (N + 1 atoms) at a rate given by [79]:

\[ Z_{Cu_N-Cu} = [Cu][Cu_N]\pi \left( \frac{\sigma_{aCu_N} + \sigma_{rCu}}{2} \right)^2 \left( \frac{8kT}{\pi \mu} \right)^{1/2}. \] (2.16)

Assuming a sticking coefficient of one, the growth rate of a N-mer will be the collision rate seen by an individual N-mer [79]:

\[ \frac{dN}{dt} = \frac{Z_{Cu_N-Cu}}{[Cu_N]} = [Cu]\pi \left( \frac{\sigma_{aCu_N} + \sigma_{aCu}}{2} \right)^2 \left( \frac{8kT}{\pi \mu} \right)^{1/2} \] (2.17)

Where \[ 1/\mu = 1/\mu_{CuN} + 1/\mu_{Cu}. \]
Finally, for a given set of processing conditions and a time of flight (τ) for the metal atoms from source to substrate, Hill suggests that the average size of clusters \(N_{av}\) in a system is given by [79]:

\[
N_{av} = \frac{1}{\tau} \int_{0}^{\tau} N(t) d\tau. \tag{2.18}
\]

While Hill has theoretically examined cluster formation rates, others like Dugdale [50] have experimentally explored how vapor phase nucleation of particle clusters affects film structure and has uncovered methods for avoiding cluster formation. Dugdale [50, 84] and others [46] have found that evaporation in low vacuum with an ambient temperature gas in the chamber can lead to homogeneous nucleation of vapor clusters and “the precipitation of powders which form friable and porous columnar structures” [50]. The parameters which determine when such structures appear include the evaporant material used, the evaporation rate, the specific ambient gas and pressure, the geometry of the system, and the temperature of the substrate [50]. Substrate heating alone does not eliminate the effects of vapor phase cluster nucleation upon microstructure. Further exploration by Dugdale [84] revealed however that the apparent effects of vapor phase cluster nucleation could be significantly reduced by heating the gas in the vacuum chamber as high as 600°C.

Dugdale [84] explained that chamber gas and vapor atom heating should theoretically decrease the vapor atom concentration, should increase the radius of a thermodynamically stable cluster [86], and should thus decrease the number of clusters which form. (The dependence of cluster formation rate upon temperature and vapor atom concentration has been examined in some detail elsewhere [86-88].) Dugdale concluded by reporting a reduction in cluster concentration as a result of heating the gas and vapor in his deposition chamber. This significantly changed film microstructure, from porous to dense columns.
While he did not suggest a physical explanation for the microstructural change, it is not difficult to envision that low energy cluster deposits form a porous material structure while individual atoms at a higher temperature create a denser microstructure (Fig. 2.5).

2.2.3. Jet Vapor Deposition™

During the 1980’s a new method was invented for creating films in a reduced vacuum and for manipulating vapor stream characteristics (i.e. distribution, energy, angle, efficiency, and form) during transport from source to substrate [47, 85]. Jet Vapor Deposition™ (JVD™) used a nozzle and gas jet to transport atoms or clusters of atoms to a substrate for deposition. This technique represents an extension of the technology of high pressure ratio molecular beam separators to a lower pressure ratio regime [101-110].

JVD™ often employs either a thermal evaporation source (a resistively heated wire) or another non-electron-beam heating source in combination with an inert gas jet to create

Figure 2.5  **The effect of clustering upon deposited film morphology.** A hypothetical comparison between the film structure formed during low energy cluster deposition and higher energy individual atom deposition.
vapor atoms, to accelerate those atoms from their thermally induced velocities, to concentrate the vapor stream through a spray nozzle, and to deposit the adatoms onto a substrate in a low vacuum (~ $10^{-2}$ Pa) (Fig. 2.6) [9, 10, 12]. JVD$^\text{TM}$ employs vapor atom collisions with a carrier gas flowing towards the nozzle exit to redirect the vapor and reshape the vapor’s density distribution. Using a pressure drop into the chamber to accelerate the entire flow, the JVD$^\text{TM}$ method then makes use of the inertial momentum of the vapor atoms to create a focussed deposit since, for a critical range of pressures, many of the vapor atoms cannot be turned into the wall jet by atomic collisions with the carrier gas before contacting the substrate (Fig. 2.6).

Figure 2.6 **Molecular beam deposition.** Once vapor atoms are accelerated through a nozzle, they can either impinge upon the substrate or be deflected into the wall jet. The pressure ratios shown are representative of those employed in a JVD$^\text{TM}$ system [12, 79].
Reported results from deposits created with molecular beam separators and JVD\textsuperscript{TM} processes suggest that they could have a unique ability to vary vapor atom spatial, angular, and energy distributions as well as deposition efficiencies and vapor atom forms [47, 80, 83, 101-112]. Though not reporting exact distribution information, JVD\textsuperscript{TM} results indicate that, by using a high molecular weight vapor atom / low molecular weight carrier gas combination (e.g. gold / helium), focussed, highly efficient, highly nonuniform deposits can be created on stationary substrates [47]. While reporting focussed, high deposition efficiencies for gold on flat substrates (95%), Halpern et al. [47] and others [113, 114] do not provide information on the exact vapor atom spatial, angular, or energy distributions during transport and deposition. Hill [79] does present limited fiber coating deposition distribution data for the JVD\textsuperscript{TM} process with basic continuum-based model explanations for the observed experimental results. In other modeling work related to the JVD\textsuperscript{TM} process, de la Mora et al. [115] and Marple et al. [104] use continuum fluid flow concepts such as Stokes number and drag coefficient to examine the influence of vapor cluster mass upon deposition efficiency. Little in-depth analysis appears to be available in the literature though for a complete assessment of the rapid material synthesis abilities of these low pressure molecular beam systems.

In addition to an ability to affect vapor atom deposition efficiency and distribution, molecular beam separators and the JVD\textsuperscript{TM} process could have the ability to increase adatom kinetic energy by passing the vapor through a nozzle. First order estimates of the maximum velocity attainable through use of a nozzle can be determined using one-dimensional equations for isentropic flow of a compressible fluid [116]. The important governing relationships between pressure, temperature, Mach number, and jet velocity are given by:

\[
\frac{P_o}{P_d} = \left[ 1 + \frac{\gamma - 1}{2} M^2 \right]^{\gamma/(\gamma - 1)}
\]  (2.19)
and

\[ U = M \sqrt{\frac{\gamma R_s T}{\gamma R_s T}} \]  

(2.20)

where

- \( P_o \) = Upstream pressure before the nozzle (Pa),
- \( P_d \) = Downstream pressure at the nozzle or in the chamber (Pa),
- \( \gamma \) = Ratio of specific heats (5/3 for helium and argon),
- \( M \) = Flow’s Mach number,
- \( U \) = Carrier gas stream speed (m/sec),
- \( T \) = Absolute temperature (K), and
- \( R_s \) = Specific gas constant (2077 J/(kg K) for helium, 208.1 J/(kg K) for argon).

### 2.2.4. Supersonic gas jet structure

While equations (2.19) and (2.20) give an upper bound to vapor atom velocity and kinetic energy exiting a molecular beam nozzle, multidimensional shock waves further downstream in low vacuum supersonic gas jets slow the carrier gas from supersonic velocities as the gas and vapor travel toward the substrate [117], making vapor atom velocity and position prediction with these one-dimensional equations impossible (Fig. 2.7). Two of the most important features of a supersonic nozzle expansion are the so-called zone of silence, where the gas flow accelerates to supersonic velocities, and a Mach disk, at which the gas flow rapidly decelerates to velocities below Mach 1 (Fig. 2.7). In addition to these structures, Adamson and Nicholls and others [117, 118] note that when a supersonic jet exits into a low vacuum (above a pressure of ~1 Pa), weak secondary shock structures can be present downstream of the sharply defined Mach disk.
The initial, expanding zone of silence is formed when the "high" pressure gas in the nozzle enters the chamber and expands in an attempt to match the lower background pressure found in the processing chamber. In many instances in which the background pressure is high enough to allow for a continuum description of atomic interaction, the nozzle exhaust overexpands, creating a lower pressure in the zone of silence than that found in the surrounding chamber. As a result, the background pressure forces the overexpanded barrel shock to narrow.

Figure 2.7 **Structure of a continuum free-jet.** The general structure of a continuum free-jet expansion has been well characterized [117-120]. The structure shown here is considered to be continuum-based since its existence requires a high enough density and collision frequency to allow for the definition of density and equilibrium temperature within the length scale of the apparatus [118].
At some point downstream, the compression waves surrounding the barrel shock coalesce to generate a diamond shock or a Mach disk shock if the pressure ratio \( P_o / P_d \) is significantly above the level necessary to generate supersonic flow (2.05 for helium and argon). Depending upon the pressure in the processing chamber, this expansion and contraction sequence can be repeated as the jet attempts to reach equilibrium with the surrounding gas. Subsequent shock waves beyond the initial Mach disk are of decreasing strength as viscous effects dissipate the jet’s energy [117]. While the zone of silence represents the primary region of supersonic flow, the repeated expansions of the jet downstream can create small additional regions of supersonic flow. The final major feature of the flow is the wall jet. Once the gas flow interacts with the substrate, the speed of the gas jet toward the substrate slows dramatically, a concave wall shock forms, and the gas is forced parallel to the substrate [120]. In sum, the idea of using a carrier gas stream to facilitate vapor deposition appears intriguing, but the technique is not well characterized or understood.

Interaction of the vapor atoms and carrier gas with the substrate undoubtedly decreases the adatom velocity component directed toward the substrate as the vapor atoms are redirected into the wall jet (c.f. Fig. 2.6). While the correlation between velocity and kinetic energy for vapor atoms of selected mass is simple \( E = \frac{1}{2}mv^2 \), little experimental or theoretical work has been done to determine the actual velocity of adatoms reaching the surface in a vapor deposition system utilizing a nozzle and gas jet.

2.2.5. Vapor transport modeling

Because of the development of low and medium vacuum technologies such as diode sputtering and JVD™, theoretical understanding of vapor transport for materials processing has become a point of focus in recent years. Numerous researchers have investigated vapor transport issues in these systems and have realized that modifications to initial
vapor stream characteristics result from collisions with gas atoms in the processing chamber which affect vapor deposition properties of the system (e.g. depositing atom energy, angle, and distribution) [121-137]. To understand the significance of vapor transport effects upon material deposition characteristics and to optimize the design of vapor deposition systems operating in medium or low vacuum, researchers have three primary avenues along which to investigate the phenomena: solution of the Navier-Stokes equations, solution of the Boltzmann equation, or direct physical simulation of the gas flow.

The Navier-Stokes equations [116] are a set of partial differential equations that represent the equations of motion governing a fluid continuum. While in actuality a fluid flow represents collision events between the individual atoms of a gas or liquid flow, under many conditions the Navier-Stokes equations allow the properties to be defined and solved for in a continuum (average) sense. One form of the Navier-Stokes equations is shown below in Einstein’s tensor notation [138]:

\[ \frac{\partial p}{\partial t} + \frac{\partial}{\partial x_j} \rho u_j = 0 \]  
(2.21)

\[ \rho \frac{\partial u_i}{\partial t} + \rho u_j \frac{\partial u_i}{\partial x_j} = -\frac{\partial p}{\partial x_i} + \frac{\partial \sigma_{ji}}{\partial x_j} \]  
(2.22)

\[ \rho \frac{\partial H}{\partial t} + \rho u_j \frac{\partial H}{\partial x_j} = \frac{\partial p}{\partial t} + \frac{\partial}{\partial x_j} (\sigma_{ji} u_i - q_j) \]  
(2.23)

where  
\( t \) = Time (sec),  
\( x_i \) = Position (m),  
\( u_i \) = Velocity (m/sec),  
\( \rho \) = Density (g/cm\(^3\)).
\[ P = \text{Pressure (Pa)}, \]
\[ H = \text{Total enthalpy (kJ)}, \]
\[ \sigma_{ji} = \text{Viscous stress tensor (Pa)}, \text{and} \]
\[ q = \text{Heat flux (W)}. \]

Whether or not it is appropriate to use the Navier-Stokes equations to analyze a fluid flow problem is determined through calculation of the dimensionless Knudsen number (Kn) of a flowfield [116]:

\[
(Kn) = \frac{\lambda}{L} \tag{2.24}
\]

where \( \lambda = \text{Mean free path (m)}, \) and
\[ L = \text{Characteristic dimension of the modeled geometry (e.g. source to substrate separation) (m)}. \]

As laid out by John [139] and Shames [140], a Knudsen number greater than 0.1 represents the transition to free molecular flow at which point a Boltzmann equation solution or discrete atom simulation must be employed rather than the continuum Navier-Stokes equations. To estimate the validity of continuum based computations, a quick calculation of \( \lambda \) can be made using the following equation [126, 141]:

\[
\lambda \equiv \frac{1}{\pi d^2 n} \tag{2.25}
\]

where \( d = \text{Gas atom hard-sphere diameter (m)}, \) and
\[ n = \text{Gas atom number density (atoms/m}^3). \]
(The source of equation (2.25) will be explored extensively later in the dissertation - section 8.2.2.)

While several researchers have used the Navier-Stokes equations to examine vapor transport for materials synthesis [112, 125, 142] there are drawbacks to use of these equations. First, the continuum method does not provide information about individual atoms as desired for simulations of film growth [29-33]. Second, the Navier-Stokes equations which most commercial continuum codes employ often have difficulty capturing the phenomena associated with vapor transport at many of the rarefied processing pressures utilized [116, 139]. As Shames notes [140]:

> The continuum breaks down when the mean free path of the molecules is of the same order of magnitude as the smallest significant length in the problem [e.g., nozzle diameter in a JVD trademark system]. Under such circumstances we may no longer detect meaningful, gross manifestations of molecules. The action of each molecule or group of molecules is then of significance and must be treated accordingly.

In a slightly different explanation Bird [141] goes on to note that the Navier-Stokes equations can no longer be used once it becomes impossible to relate average values of appropriate molecular quantities such as shear stresses and heat fluxes to macroscopic quantities such as pressure, temperature, and velocity. According to Bird [141]:

> More specifically, the transport terms in the Navier-Stokes equations of continuum gas dynamics fail when gradients of the macroscopic variables become so steep that their scale length is of the same order as the average distance travelled by the molecules between collisions, or mean free path.

An alternative to the use of the Navier-Stokes equations is solution of the older Boltzmann equation dating from 1872 which can be used to describe molecular behavior in a fluid
over a much wider range of Knudsen numbers, from Kn less than 0.001 to Kn greater than 100 [141]. The Boltzmann equation is shown below [143]:

\[
\frac{\partial f}{\partial t} + u_j \frac{\partial f}{\partial x_j} + F_j \frac{\partial f}{\partial u_j} = \frac{\partial f}{\partial t}
\]

where  \( f \) = Velocity distribution function of a gas,

\( u \) = A single atom’s velocity function, and

\( F \) = Some external force acting upon the gas atom at time \( t \).

(The right side of the equation represents the change in the velocity-distribution function for the total gas with time as the result of binary collision encounters \((e)\) at a fixed point. Chapman and Cowling [143] provide a thorough explanation of the origin of this equation.) The major drawback to using the Boltzmann equation for analysis of vapor transport has been the difficulty of obtaining solutions to the complex equation. A notable exception is the Chapman-Enskog solution of the Boltzmann equation for “a restricted set of problems in which the distribution function \( f \) is perturbed by a small amount from the equilibrium Maxwellian” distribution [141]. Solutions such as Chapman-Enskog will not always be valid in material processing systems where gas atom velocities are far from Maxwellian, e.g. supersonic gas expansion from a nozzle.

To attack problems of this type, researchers have turned to direct physical simulations of the gas flow in which computers are used to calculate the interaction of many thousands or even millions of representative atoms as they collide with one another or interact with boundaries in simulated physical space. Solutions for both steady and unsteady state problems are obtained by averaging over many small time steps. Some of the most recent vapor transport material processing modeling efforts of this type have been produced by Elsing, Knotek and others [121-124] in which vapor transport in diode sputtering has been
simulated. While providing a hint of the type of adatom deposition energy and angle information which can be produced by direct physical simulations of vapor transport, these initial efforts have been limited.

Proper theoretical description of the individual collision processes requires the use of interatomic potentials, energy dependent atomic cross-sections, and classical mechanics describing the collision of two bodies moving in three dimensions [58, 126-136, 144]. Elsing, Knotek, and others [121-124] have not employed any of these basic concepts in their models. In addition, their sputtering results assume that the gas atoms are stationary during collisions with energetic vapor atoms. Finally, they base their adatom energy and angular distribution conclusions upon the simulation of a limited number of atoms (~100), a number too small to eliminate statistical fluctuations from the results [137]. Simulation of just 100 atoms by Elsing and Knotek highlights one of the primary drawbacks to stochastic modeling of individual atom collisions, the computational expense of trying to track the many moles of atoms actually involved in vapor transport.

One of the more fully developed methods of direct physical simulation of thousands or millions of atoms in a gas flow is the Directed Simulation Monte Carlo (DSMC) method originally developed by G.A. Bird [141]. This method has been used extensively in recent years and has built a solid reputation as a modeling tool through comparisons of model results with independent laboratory experiments [120, 141, 148-151] for a number of engineering problems, including vapor transport [147, 148]. While providing reasonable accuracy, the DSMC method tries to minimize the computational expense of direct physical simulations by making certain approximations such as the use of variable hard sphere (VHS) and variable soft sphere (VSS) estimates of atomic dimensions rather than more accurate, but computationally expensive, estimates of energy dependent atomic cross-sections [141]. There are some indications that these estimates lead to discrepancies between
model and experiment \cite{152, 153}. Bird \cite{141} discusses that the problem with the VHS approximation is that “this scattering law is not realistic and that the cross-section is independent of the relative translational energy $E = \frac{1}{2}mv^2$ in the collision. Other than at extremely low temperatures, the effective cross-section of real molecules decreases as $c_r$ [velocity] and $E_I$ increase.” Bird also notes that even when the more sophisticated VSS model is invoked “the diameter varies in the same way as the VHS model, but the deflection angle is...” given somewhat more accurately.

In general though, use of the general DSMC method to model low vacuum vapor transport could provide a vital link between current understanding of vapor creation and general vapor deposition characteristics in this environment. Indeed it is probably the preferred method of simulation for studying the vapor transport problem due to its reliance upon a direct physical simulation of the problem, an approach valid at all mean free path lengths encountered in medium or low vacuum vapor transport. Reliance upon continuum methods could introduce severe uncertainty into results. The flow structure shown in Fig. 2.7 not only has significant changes in Mach number associated with various portions of the gas flow but also large changes in pressure and mean free path \cite{110, 118}. While continuum equations could be valid in one portion of the flowfield, they could be quite inaccurate in others. Reliance upon DSMC methods, based on discrete particle concepts valid across the entire important range of Knudsen numbers, appears to be justified. Accurate prediction of deposition distributions, energies, impact angles, efficiencies, and forms with DSMC methods could provide accurate input to molecular dynamics and Monte Carlo simulations of vapor adsorption and diffusion on a substrate for the design of engineering structures \cite{29-33}.
2.3 Vapor Adsorption and Diffusion on a Substrate

The ultimate motivation for creating and transporting vapor to a substrate is the formation of useful engineering products from the vapor phase. Extensive research to date [12, 29-33, 61, 68, 154-182] has already provided great insight into what vapor creation and transport based processing parameters affect vapor phase material structural development. Although microstructure formation will not be a focal point of this dissertation’s research, the generation of desired, useful microstructure is ultimately the reason for developing a system which can manipulate vapor atom transport characteristics.

The desire to create films repeatedly and economically and to understand how the entire deposition process determines the film microstructure and properties has led researchers to explore film growth through experiments [12, 68, 154-173] and computer-aided modeling [29-33, 61, 174-183]. Much of this work has focussed upon understanding what determines the occurrence of point, linear, and planar defects during film nucleation and growth, the presence of chemical imperfections, and the formation of amorphous, polycrystalline, or single crystal deposits - all critical microstructural variables affecting the final physical properties of films in engineering applications. Many of the contributors to Bunshah’s book note [12] agree that the most important factors affecting vapor phase material growth are:

- Elemental composition of the depositing atoms [156],
- Film growth temperature [66, 155],
- Deposit thickness [65],
- Substrate material [1], cleanliness [183], crystallinity [1], and orientation [1, 61],
- Rate of deposition [66, 174],
- Kinetic energy of the atoms landing on the substrate [30, 179],
As these parameters have been identified, efforts have focused upon the development of processing roadmaps which can aid engineers as they design film synthesis equipment by showing the influence of the various parameters upon microstructure (e.g. Figs. 2.8 and 2.9). Both figures show how several of the factors listed above affect film microstructure.

The underlying cause of a significant portion of the reported microstructure variation appears to be the directed energy of the adatoms. In Fig. 2.8, as chamber pressure increases, vapor atom thermalization becomes greater, and, as Zhou et al. [31] explain, adatoms depositing with lower energies and at normal incidence have a limited ability to...
move across the film surface to form a dense microstructure. Similarly, decreasing the substrate temperature makes less energy available to depositing adatoms. As a result, their ability to jump from one site on the surface to another is minimized, again leading to a more porous structure.

![Vacancy concentration as a function of adatom energy](image)

**Figure 2.9** *Vacancy concentration as a function of adatom energy.* Two dimensional molecular dynamics modeling, using an embedded atom method to describe interatomic interactions, reveals a lattice site vacancy concentration dependence upon incident Ni adatom energy; deposition rate = 10 nm/ns [31].

Both Figs. 2.8 and 2.9 highlight the dramatic changes which can be made to material structure as deposition parameters are varied. Experimental and modeling work to date has allowed many of the basic, important process-property relations to be uncovered and many significant vapor phase film processing technologies to be developed which can manipulate the important process parameters to create film products. While current technology based on this general understanding of deposition is capable of producing highly
engineered films, most researchers acknowledge that process capabilities must evolve and that process models of vapor creation, transport, and deposition, beyond the level of general film growth roadmaps, must be developed and employed during film synthesis to attain tomorrow’s more stringent specifications.

Indeed, some researchers believe vapor creation, transport, and deposition models will have to be incorporated into closed-loop, real-time process control systems (e.g. Intelligent Processing of Materials (IPM) [184, 185]) which utilize in-situ sensors throughout the process to ensure quality film creation. The work of Yang, Zhou, Johnson, and Wadley [29-33] to model deposition phenomenon represents an effort to move beyond general roadmaps and towards material design tools and eventually closed-loop control.

2.4 Summary

The preceding examination of electron beam film synthesis illustrates that e-beam systems have a strong ability to process a great number of elements, alloys, and compounds. At the same time, study of e-beam vapor deposition distributions, efficiencies, angles, and energies reveals that, for certain applications, an ability to chose the desired range of these parameters for different applications could enhance the attractiveness of electron beam systems to material processors.
Chapter 3

Invention of Directed Vapor Deposition

Having surveyed the state-of-the-art in electron beam processing and having reviewed various methods for the modification of e-beam material creation characteristics, it appeared that an opportunity did indeed exist for the enhancement of electron beam material synthesis characteristics. The desire was to develop a method which could deposit refractory elements, compounds, and alloys onto complex shapes by a rapid, efficient, and low contamination method capable of line and non-line-of-sight coating. The literature reviewed in Chapter 2, specifically section 2.2.2., indicated that non-line-of-sight could be achieved by synthesizing material from the vapor phase in low vacuum. However, deposition efficiencies in this environment were reported to be generally lower than in high vacuum systems. Still, the literature reviewed in section 2.2.3. suggested that improved vapor stream focus and deposition efficiency could be achieved by not only synthesizing vapor phase materials in a medium or low vacuum but also by using a carrier gas stream as a means of transporting vapor to the deposition surface.

Thus, in a departure from conventional electron beam (e-beam) evaporation methods [2, 11, 37] which create atomistic vapor in high vacuum (10^{-6} - 10^{-2} Pa / 10^{-8} - 10^{-4} Torr), a
new low vacuum e-beam based physical vapor deposition system, termed Directed Vapor Deposition (DVD), is proposed. This new method uses an e-beam in a low vacuum environment \((10^{-1} - 10^3 \text{ Pa} / 10^{-3} - 10 \text{ Torr})\) where a carrier gas stream can be utilized to entrain evaporants within that stream for efficient transport to and deposition on a substrate (Fig. 3.1) [186]. As conceived, the DVD system is the only e-beam system which seeks to capture evaporant in a reactive or inert carrier gas stream for transport to a surface (substrate) where deposition of either the pure vapor atoms or their reaction products, created in combination with carrier gas molecules, can occur [2, 11, 12, 13].

Figure 3.1  A preferred embodiment of Directed Vapor Deposition. In a Directed Vapor Deposition system, e-beam evaporant from a crucible is transported to a substrate in a carrier gas stream.
Chapter 3. Invention of Directed Vapor Deposition

The Directed Vapor Deposition system represents an attempt to build upon the well documented material processing capabilities of electron beams [11] by placing e-beam evaporated material in a new environment, a medium or low vacuum gas stream. By introducing vapor into this flow, it could be possible to synthesize materials and microstructures from the vapor phase which have so far proven to be difficult to create via other methods. The subsequent work described in this dissertation focuses upon understanding the interaction of e-beam evaporant with a gas stream as a mechanism for creating engineered materials. Once this work has provided some initial insight into this interaction, it should be possible to focus future technology development of this type upon the areas of materials synthesis which hold greatest promise.

As noted in the Background chapter, the process of vapor phase material synthesis consists of five steps:

1. Creation of the vapor.
2. Transport of the vapor to the substrate.
3. Adsorption of the vapor onto the substrate.
4. Diffusion of the adatoms across the substrate surface.
5. Movement of the adatoms by bulk diffusion through the film lattice to their final positions.

While the DVD film synthesis method will follow these general process steps, there are several aspects of its specific approach to processing which could combine to present opportunities for economic, high quality materials synthesis not available with other processes. Thus, this new processing pathway, Directed Vapor Deposition, deserves to be investigated.
The intriguing, possible material processing features which could make DVD useful include the following:

- DVD should entrain and focus vapor atoms in a carrier gas stream. This feature could make it possible to change the distribution and angle of deposition for vapor atoms reaching the substrate. In applications where material is to be deposited over a small area (e.g. fiber coating for composite applications), DVD focussing of the vapor stream could greatly enhance material utilization efficiency, decrease production time, and lower final product cost. In applications where material is to be deposited onto uneven surfaces or surfaces with recessed regions (e.g. semiconductor via filling applications), changing the angle of the vapor stream could enhance surface coverage or feature filling [69, 76].

- The lower portion of the DVD vacuum pressure regime is comparable to that found in diode sputtering systems. As researchers [144, 188] have observed, the mean free path\(^1\) of the vapor atoms in this environment is short enough to result in significant vapor atom scattering and redirection in the processing chamber as a result of collisions with carrier gas atoms. Consequently, DVD should exhibit a similar high throwing power\(^2\) when compared to high vacuum deposition techniques [12, 50], leading to more efficient materials utilization, faster processing, and lower final product cost when depositing material onto curved or uneven surfaces.

- For those material systems which are difficult to process in conventional e-beam or sputtering systems, DVD’s use of a gas jet may facilitate mixing of vapor from different sources, allowing otherwise difficult to synthesize compounds and alloys to be fabricated rapidly. Material systems with widely different vapor pressures represent one area where DVD may provide important processing advantages (e.g. the addition of hafnium to nickel aluminide bond coat layers during TBC synthesis).

---

1 mean free path - average distance between collisions with other atoms.
2 throwing power - ability to deposit vapor onto substrate surfaces that are not in the line-of-sight of the vapor source.
• If the carrier gas jet exits the flow tube (Fig. 3.1) with a high enough velocity, DVD atoms subsequently captured in the carrier gas stream should be accelerated. If acceleration occurs, the vapor atoms could impinge upon a substrate surface with 0.5 - 2 eV of kinetic energy. Such energy levels are comparable to the activation energy for surface diffusion [190]. Thus DVD adatoms could possess enough energy to increase their surface diffusion rates to low energy sites above levels observed with established thermal evaporation methods. Substrate bombardment by energetic carrier gas atoms might also aid in beneficial atomic rearrangement in a growing film [29 - 33]. While increasing adatom energy from thermal levels of 0.1 - 0.2 eV to enhanced energy levels of 0.2 - 2 eV, the DVD method should not raise energy levels to the point where substrate damage [191] or material sputtering can occur [16], as in ion plating.

• If DVD can enhance adatom kinetic energy, there will also exist an increased possibility of athermal atomic reconstruction at the growth surface as the result of impacting energetic vapor atoms moving across the substrate surface before settling in a preferred low energy surface site. Thus the DVD process could construct useful microstructures at reduced substrate temperatures, thereby reducing the importance of bulk diffusion. The ability to synthesize film products at reduced substrate temperatures could be critical to economic fabrication of numerous products (e.g., flat panel displays) (See section 1.2.).

• The creation of e-beam evaporant in a low or medium vacuum provides a natural environment for reactive deposition which combines elements normally in the vapor phase with those in the solid phase. Since DVD introduces gas into the processing chamber as part of its standard material synthesis routine, the DVD material synthesis environment will hopefully be able to produce not only pure materials but also compounds created via vapor / gas interaction during transport to the substrate. Compounds difficult to process in high vacuum could be more easily created in a reactive DVD carrier gas jet (e.g. yttria-stabilized ceria for thermal barrier coatings (TBCs)).
• The DVD process should take advantage of the high rate, energy efficient evaporation capability of electron beams [11]. Electron beam systems have demonstrated an ability to process a large array of pure metals, alloys, and compounds and to deposit material at rates as high as 1 mm/min over hundreds of square centimeters. In an industrial setting, high product throughput and economic power utilization can be keys to a process’ viability.

• The processing vacuum of DVD should be conducive to rapid batch or continuous material synthesis. While utilizing the well characterized electron-beam evaporation tool, DVD will operate this tool in a low vacuum environment, a distinct departure from conventional e-beam processing. As a result DVD will be able to employ high pumping capacity rotary piston pumps with mechanical boosters. These pumps are able to evacuate the synthesis chamber to process vacuum in less than two minutes, a significantly shorter time than the 20 minutes to 3 hours required by high vacuum diffusion or cryogenic pumps utilized in conventional, reactive evaporation (RE), or activated reactive evaporation (ARE) e-beam deposition systems [192, 193]. In an industrial setting, a decrease in product synthesis time directly correlates with a decrease in product cost.

In sum, should the DVD system conceived of in this chapter demonstrate an ability to create useful materials economically, it could become a valuable tool for the manufacture of products as varied as thermal barrier coatings for aircraft turbine blades, polycrystalline silicon deposits for thin film transistors, and metal matrix composites for high temperature structural applications.
Chapter 4

DVD System Design

In its most basic form (Fig. 3.1), the proposed Directed Vapor Deposition (DVD) system will consist of four primary components: a source of material to be evaporated, a means of creating an atomistic vapor from the source, a flow of carrier gas in which the atomistic vapor is transported through the processing chamber, and a substrate upon which the vapor deposits. As discussed in Chapters 1, 2, and 3, an electron beam gun was identified early in the technology development process as the desired source material evaporation tool because of its ability to vaporize refractory (i.e. high melting point) materials rapidly and cleanly. To create a basic but effective demonstration of the DVD concept, the design work described in this chapter seeks to integrate e-beam technology into a low vacuum processing environment where the vapor stream generated by the e-beam from a crucible can be captured in a carrier gas stream for transport to a chosen substrate. Central to this design approach is the thought that placing e-beam evaporant in a carrier gas stream might improve the vapor stream’s characteristics for specific applications (e.g., spatial, angular, and energy distribution as described in the Background chapter), making the technology an important vapor phase material synthesis tool. This chapter describes the trade-offs in specifications of the many DVD system components which will fit together to form the
DVD material synthesis tool. As the work of this chapter will demonstrate, detailed analysis of the basic idea laid out in Chapter 3 is required before the DVD concept can be reduced to practice in a functioning material processing system.

4.1 Electron Beam Gun

Although most electron beam gun technology has been developed to operate in systems in which both the gun and processing chamber are maintained at medium or high vacuum, the Background chapter (section 2.1.3.) noted that there exists no scientific barrier to employing an e-beam gun in a system which maintains a low vacuum in its processing chamber, as desired for the DVD system. To create such a system capable of processing refractory materials at high rates, numerous analyses must be made before a gun for the DVD system can be specified. The primary design issues for the gun include specification of the maximum power generation capability and the required e-beam accelerating voltage, selection of the beam generation mechanism, and choice of desired e-beam characteristics (e.g. beam diameter and scanning radius/rate).

4.1.1. Maximum e-beam gun power requirements

Specification of the maximum e-beam gun power capability for new (high or low vacuum) evaporation systems is challenging because of the uncertainty involved in determining the magnitude of the various e-beam energy losses between generation of the beam and generation of the vapor. The amount of e-beam energy actually available for material evaporation in a DVD system depends upon the energy losses which include those described in various references [11, 37] as well as additional energy sinks resulting from the low-vacuum DVD operating environment:
• Inside the gun due to some fraction of the beam impinging on various portions of the gun,

• In the gas and vapor cloud due to electron scattering collisions,

• From the evaporant material surface as a result of electron backscattering,

• Through conduction into the crucible containing the melt material,

• From the radiating molten evaporant surface, and

• Through convection caused by the gas jet blowing across the evaporant surface.

Schiller [11] and Storer [21] have indicated that, in a conventional high vacuum e-beam system employing a water-cooled crucible, the standard energy sinks listed above can lead to as little as 10% of the initial beam power actually being transformed into source material evaporation energy. Calculation of a necessary e-beam gun power capability for the DVD system assumed that even less of the initial beam power, as little as 3 - 3.5%, would actually contribute to material evaporation. This small number was selected for gun power calculations since energy losses in the DVD system should exceed those in a conventional e-beam system due to increased beam dissipation inside the gun and in the low vacuum environment and due to gas jet convection.

One of the materials of primary interest for fiber coating in the e-beam DVD system was titanium. An e-beam power calculation was undertaken to determine how powerful an e-beam gun would be required to deposit titanium in the DVD system. This calculation assumed that the temperature of the melt had to be raised to the material’s boiling point. In fact, studies have shown [11] that controlled e-beam evaporation typically occurs below the material’s boiling point at a source vaporization temperature ($T_v$) which induces an equilibrium vapor pressure of about 1 Pa. During calculation of the power requirement results of Table 4.1, determination of $\Delta H$ up to a vapor pressure of 1 Pa rather than the boiling point generally decreased the power required by about 10%. However, given the
uncertainties in power losses throughout the system, using the boiling point rather than the 1 Pa vapor pressure point was considered an acceptable safety factor.

Table 4.1: Thermophysical data

Calculation of power required to evaporate materials in the DVD system [194, 195].

<table>
<thead>
<tr>
<th>Elements</th>
<th>At. Wt. (g/mol)</th>
<th>Density (g/cm$^3$)</th>
<th>$T_m$ (K)</th>
<th>$T_b$ (K)</th>
<th>$c_p$ (J/K mol) solid</th>
<th>$c_p$ (J/K mol) liquid</th>
<th>$L_f$ (kJ/mol)</th>
<th>$L_e$ (kJ/mol)</th>
<th>$\Delta H$ (KJ/mol)</th>
<th>Power (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>27.0</td>
<td>2.70</td>
<td>933</td>
<td>2793</td>
<td>20.7</td>
<td>12.3</td>
<td>10.4</td>
<td>290</td>
<td>372</td>
<td>6.4</td>
</tr>
<tr>
<td>Cu</td>
<td>63.6</td>
<td>8.96</td>
<td>1356</td>
<td>2840</td>
<td>22.6</td>
<td>5.6</td>
<td>13.0</td>
<td>306</td>
<td>350</td>
<td>8.5</td>
</tr>
<tr>
<td>Mo</td>
<td>95.9</td>
<td>10.2</td>
<td>2893</td>
<td>4880</td>
<td>24.1</td>
<td>1.2</td>
<td>35.5</td>
<td>590</td>
<td>744</td>
<td>14</td>
</tr>
<tr>
<td>Ni</td>
<td>58.7</td>
<td>8.90</td>
<td>1726</td>
<td>3180</td>
<td>17.0</td>
<td>29.5</td>
<td>17.2</td>
<td>375</td>
<td>498</td>
<td>13</td>
</tr>
<tr>
<td>Nb</td>
<td>92.9</td>
<td>8.57</td>
<td>2740</td>
<td>5010</td>
<td>23.7</td>
<td>4.0</td>
<td>29.3</td>
<td>681</td>
<td>498</td>
<td>10</td>
</tr>
<tr>
<td>Si</td>
<td>28.1</td>
<td>2.33</td>
<td>1683</td>
<td>2628</td>
<td>23.9</td>
<td>2.5</td>
<td>50.7</td>
<td>386</td>
<td>659</td>
<td>6.8</td>
</tr>
<tr>
<td>Ti</td>
<td>47.9</td>
<td>4.54</td>
<td>1940</td>
<td>3560</td>
<td>22.1</td>
<td>10.0</td>
<td>17.5</td>
<td>427</td>
<td>475</td>
<td>9.0</td>
</tr>
<tr>
<td>V</td>
<td>50.9</td>
<td>6.11</td>
<td>2188</td>
<td>3680</td>
<td>20.5</td>
<td>10.8</td>
<td>16.7</td>
<td>456</td>
<td>550</td>
<td>12</td>
</tr>
<tr>
<td>Y</td>
<td>88.9</td>
<td>4.47</td>
<td>1803</td>
<td>3573</td>
<td>23.9</td>
<td>7.55</td>
<td>11.4</td>
<td>371</td>
<td>575</td>
<td>4.4</td>
</tr>
<tr>
<td>Zr</td>
<td>91.2</td>
<td>6.51</td>
<td>2130</td>
<td>4673</td>
<td>22.0</td>
<td>11.6</td>
<td>19.3</td>
<td>575</td>
<td>661</td>
<td>8.1</td>
</tr>
</tbody>
</table>

$c_p$ = Specific heat at constant pressure  
$L_f$ = Latent heat of fusion  
$L_e$ = Latent heat of evaporation

The e-beam gun power required to evaporate some material at a specified rate can be determined using the data of Table 4.1 and the following equation [11]:

$$W = \frac{r_e \Delta H}{Ve}$$  \hspace{1cm} (4.1)

where  
$W$ = Power required (W),  
$r_e$ = Evaporation rate (m$^3$/min),
\[ \Delta H = \text{Enthalpy required to raise material from room temperature to evaporation temperature (kJ/mol)} \]

\[ V = \text{Molar density of material (m}^3/\text{mol)} \]

\[ \varepsilon = \text{Efficiency of energy utilization (3 - 3.5\%)} \]

For titanium deposition using DVD, the following material deposition parameters were specified based upon general industry specifications for the MMC application [20]. The gun should be capable of depositing material at a rate of 10 - 15 \( \mu \text{m/min} \) [21] onto 10 meters of 140 \( \mu \text{m} \) diameter, rotating fiber (e.g. SCS-6 SiC fibers rotating at 10 rpm) at 20\% deposition efficiency. (All of these numbers factor into a determination of \( r_e \), the evaporation rate required in the system.) Calculation shows that about 9 kW of initial beam power would be required to evaporate titanium for the desired rate of coating. As a result of this calculation, a 10 kW gun was specified. For comparison, the power required to coat an identical substrate with other materials is shown at the bottom of Table 4.1.

4.1.2. Accelerating voltage selection

Although the calculations of the previous section produce a reasonable gun power specification, that specification is based on several assumptions: deposition efficiency (20\%) and energy utilization efficiency (3 - 3.5\%). Refining the deposition efficiency specification is difficult because a DVD system does not yet exist to coat fibers and determine the material utilization capabilities of the system. The energy utilization efficiency is also difficult to quantify without an actual system to analyze. However, to ensure that the gun can evaporate material at a rate greater than or equal to that which is desired, energy utilization efficiency can be maximized through the choice of an appropriate e-beam accelerating voltage which will minimize e-beam energy dissipation during travel from cathode to target. As noted in section 2.1.3., the actual beam power transmitted to the evaporation mate-
rial will be less than 10 kW due in part to beam energy dissipation as a result of atom / electron scattering interactions in the gun and chamber. The discussion in the Background section noted that increasing the accelerating voltage and thereby decreasing the scattering cross-section of the atoms in the chamber would increase beam propagation through the low vacuum. To ensure an ability to evaporate rapidly even high melting point materials (e.g. graphite, tungsten, and molybdenum), an accelerating voltage / carrier gas combination should be chosen which will transmit as much as possible of the beam’s initial energy to the source material.

The amount of electron beam scattering which occurs between the initial electron source and the final target depends upon the number of gas atom / electron interactions which occur (i.e. the gas pressure in the chamber), the range of the gas atom / electron interaction potential (Range increases with gas atom atomic number.), and the length of time over which the electron is acted upon by the interaction potential. This final element, length of time, is directly proportional to the velocity of the electrons in the beam where the velocity is determined by the accelerating voltage utilized in the gun (Higher accelerating voltages correspond to higher velocities.). Arata [49] has proposed equations, based upon experimental study, which describe electron-beam penetration through an inert gas with reasonable accuracy using a modified Bethe stopping power formula. (The Bethe range is considered to be the total distance that the beam’s electrons can travel through the gas before losing all of their energy [48].) The expression proposed by Arata [49] was:

\[ B = B_o \left( 1 - \frac{h}{R_e} \right)^{1/2} \]  

(4.2)

where  

\( B \) = Beam voltage at distance \( h \) (m) from nozzle exit (kV),

\( B_o \) = Initial beam voltage (kV), and
\[ R_e = \text{Electron range (m)}. \]

\( R_e \) is a complicated function of the initial electron energy, the classic radius of an electron, and the temperature, density and atomic number of the gas in the chamber [49]. Equation (4.2) assumes that the gas density is constant along the e-beam path and that “above a certain fractional energy transfer, \( \varepsilon_1 \), the atomic electrons can be regarded as free, so that Moller’s cross section for scattering of free electrons by free electrons at rest in [sic.] Born approximation is applicable [196].” Moller’s cross-section is simply a description of the range of the interaction potential between the free electrons in the e-beam and free electrons at rest (i.e. around a gas atom nucleus).

Fig. 4.1 shows the predictions of Arata’s equation for an electron-beam propagating through various helium or argon pressures. Beam propagation through the lower atomic

\[ \begin{align*}
13.3 \text{ Pa (0.1 Torr) He} \\
133 \text{ Pa (1 Torr) He} \\
665 \text{ Pa (5 Torr) He} \\
665 \text{ Pa (5 Torr) Ar}
\end{align*} \]

Selected voltage

DVD range of interest

\[ \begin{align*}
0 & \quad 10 & \quad 20 & \quad 30 & \quad 40 & \quad 50 & \quad 60 & \quad 70 \\
10^{-3} & \quad 10^{-2} & \quad 10^{-1} & \quad 1 & \quad 10 & \quad 100
\end{align*} \]

Accelerating voltage (kV)

Propagation distance (m)

Figure 4.1 **Electron beam propagation in low vacuum.** The distinctly different electron propagation distances (Bethe ranges) in helium and argon are illustrated for ambient temperature and various pressure conditions.
number helium is superior because of the shorter range electron / atom interaction potential in that system. While the propagation of electrons through helium is clearly better, Fig. 4.1 indicates that the use of low partial pressures of other inert (e.g., argon) or perhaps even reactive carrier gases (e.g. oxygen) is feasible should it offer some processing advantage. Given the results of Fig. 4.1, helium was chosen as the primary inert carrier gas in the DVD system, and the e-beam accelerating voltage was specified as 60 kV. This accelerating voltage level was selected to afford fairly efficient beam propagation while minimizing cost and x-ray problems associated with higher accelerating voltages [11].

4.1.3. Selection of an e-beam generation source

As Schiller et al. [11] explain in their book *Electron Beam Technology*, various types of electron generating cathodes are available for use in e-beam systems, including wire, strip-type, and solid cathodes. Filaments for e-beam systems are generally made out of tungsten, a tungsten-rhenium alloy, or lanthanum hexaboride (LaB$_6$). LaB$_6$ filaments generally require vacuums of at least 5x10$^{-6}$ Torr (~5x10$^{-4}$ Pa) or better to minimize reaction with the oxygen in air. This requirement makes LaB$_6$ an unlikely material for use in the DVD system where pressures in the beam generating space could reach 8x10$^{-5}$ Torr. In addition, LaB$_6$ filaments usually generate just 10 - 100 $\mu$A of beam current [11]. Given that:

$$W = IB$$

where $I$ = Beam current (A) and  

$B$ = Beam accelerating voltage (kV),

a LaB$_6$ system with a 60 kV accelerating voltage and 100 $\mu$A of beam current would generate at most 6 W of power rather than the required 9 kW! Thus, LaB$_6$ filaments, which
are often considered superior electron emission sources in electron microscopes, were deemed unacceptable in the DVD system due to the emission current requirements of the DVD system and due to the vacuum requirements of a LaB$_6$ filament [11, 48].

For filaments made out of tungsten or a tungsten-rhenium alloy, strip-type and solid cathodes were easily eliminated from consideration. Strip-type filaments do not generate a beam of electrons, as desired for the DVD application, but rather a planar-emitting surface. Solid cathodes are generally used in much larger e-beam systems at the industrial rather than research scale (i.e., systems generating 1.2 MW of power with a beam current of 5 - 40 A, far more energy than is required for the system under design here). In consultation with e-beam gun manufacturers [197], a small-area cathode in the form of a tungsten bolt cathode surrounded by a tungsten wire cathode inside of a Wehnelt cup was selected to generate the beam electrons (Fig. 4.2). The Wehnelt cup serves to shape the initial beam generated from the bolt cathode by repelling the electrons and forcing them down through the small hole in the electric field of the cup.

During operation, the tungsten wire cathode of this system is heated electrically by passing a current until it emits electrons via thermionic emission. These electrons bombard the bolt cathode, heating it and leading to its own electron emission. Once the bolt cathode has begun to emit electrons, electron bombardment from the wire cathode in combination with direct electric current heating increases the bolt cathode temperature, increases its electron current emission density, and results in a larger emitting surface than would be achieved through bolt operation only [11]. During electron emission from the hot cathodes, a certain fraction of the tungsten is vaporized. A portion of this tungsten is then ionized by the free electrons in the system. This ionized tungsten subsequently bombards the bolt cathode leading to its erosion, depositing tungsten vapor from the bolt onto the wire cathode and Wehnelt cup, and necessitating bolt and wire cathode replacement every ten hours of oper-
4.1.4. A modified e-beam deflection system was required

In conventional e-beam gun systems, beam focusing and scanning are accomplished using electromagnets located within the body of the gun. Beam scanning is an integral feature of modern electron beam systems because it ensures rapid, uniform, controlled, atomistic evaporation from the largest possible target surface [11]. While beam focusing in a
low vacuum system can still occur inside the gun, scanning of the beam must be delayed until the beam passes through the foil window or gas flow limiting orifice separating the cathode filament from the processing chamber. This limitation of the conventional scanning system’s use in the DVD system is due to the addition of a specially-designed pressure decoupling attachment joining the gun to the processing chamber (Fig. 4.3). The

Figure 4.3 Overall e-beam gun configuration for DVD. This system combines traditional e-beam gun elements (e.g. Wehnelt cup assembly, anode, and focussing coils) with newly developed components (e.g. pressure decoupling chamber, tungsten plug and aperture, and external beam scanning coils) to create a unique evaporation tool.
decoupling chamber provides an attachment for a medium vacuum pumping system which removes most of the gas entering the gun from the processing chamber and ensures that the gas pumping capacity of the high vacuum pump at the top of the gun is not exceeded when the cross-valve, separating the high vacuum portion of the gun from the rest of the system, is opened to provide an unimpeded beam path from cathode to target.

Gas flow from the chamber into the gun is restricted at the bottom of the decoupling attachment by a tungsten plug with a 2.5 mm diameter hole which allows beam passage into the processing chamber with minimal gas flow in the reverse direction. It is this small aperture which prevents normal e-beam scan coil operation. The standard coils of the conventional e-beam gun are still present in the DVD system. However, their work is limited to minor, constant beam deflections which ensure that the beam is always passing directly down the gun’s central axis and through the small aperture in the tungsten plug. The beam is able to pass through the 2.5 mm hole in the tungsten plug because the e-beam focus coils in the gun create a minimum beam diameter of 0.4 mm just at the point where the beam enters the process chamber.

To make possible scanning of the electron beam in the DVD system, a small set of scanning coils were designed and attached to the bottom of the gun as shown in Fig. 4.3. A custom, water-cooled x-y deflection coil system was built by Deuteron, Inc. (Sherborn, MA) and coupled with a two amp digital e-beam gun sweep supply, model XYC-10, supplied by The Eddy Co. (Apple Valley, CA) to deflect the beam across a 1.27 cm diameter evaporation target [194]. The selected digital sweep supply can store up to 99 scan patterns each with up to 89 dwell points across the target from which one pattern can be selected and scanned across the surface at 0.1 - 10 Hz (Fig. 4.4). The maximum sweep angle of the e-beam can be adjusted through the e-beam sweep supply by modifying the
4.1.5. Final e-beam gun configuration

A 10kW (maximum beam power)/60 kV (constant electron accelerating voltage) e-beam gun for the DVD system was designed and built in consultation with the Fraunhofer Institute for Electron Beam and Plasma Technology (F.E.P.) of Dresden, Germany (See Appendix A for detailed design drawings). The beam current of the F.E.P. high pressure evaporator (HPE) is adjustable in 1 mA increments from 1 to 170 mA. These current adjustments correspond to power increments of 60 W. The complete package delivered by F.E.P. included a power transformer, a computer control cabinet, and the e-beam gun itself.

Figure 4.4  **A possible e-beam scanning pattern.** The strength of the two deflection coils in the DVD scanning system is varied to move the impact location of the e-beam from spot to spot on the surface of the evaporant rod stock, producing more reliable atomistic evaporation.
(Fig. 4.5). The separate beam scanning system was subsequently attached to the bottom of the gun.

Figure 4.5  **The electron beam system delivered from Germany.** The three components of the electron beam evaporator delivered by F.E.P. of Dresden, Germany. (Photo courtesy of F.E.P.)

### 4.2 Processing Chamber

A second important component of the DVD system which had to be designed and built was the vacuum chamber inside of which e-beam processing was to be performed. The primary design issues for the chamber involved 1) constructing a chamber which did not permit x-ray escape from inside the chamber out into the laboratory and 2) configuring the chamber so that multiple evaporant sources could be used to coat flat or fiber substrates.
sequentially or simultaneously. X-rays were primarily generated from electron beam interaction with the nozzle of the gun and with the evaporated source material. Although the initial system constructed for this dissertation research utilized only a single evaporant tool, provision was made in the design of the chamber to allow the option of adding two other vapor sources at a later date.

4.2.1. X-ray shielding for system user protection

The 60 kV accelerating voltage of the DVD system’s e-beam gun is capable of generating x-rays from the lightest elements up to the Kα₁ x-ray of tungsten (energy = 59.32 KeV) [48, 198]. To protect individuals near the system during its operation, the walls of the processing chamber had to be designed to absorb these x-rays. Goldstein et al. [48] succinctly explain the basic mechanism of x-ray absorption:

“X-rays as photons of electromagnetic radiation can undergo the phenomenon of photoelectric absorption upon interacting with an atom. That is, the photon is absorbed and the energy is completely transferred to an orbital electron, which is ejected with a kinetic energy equal to the photon energy minus the binding energy (critical ionization energy) by which the electron is held to the atom. X rays can also be lost due to scattering.... Photoelectric absorption by electrons in a specific shell requires that the photon energy exceed the binding energy for that shell. When the photon energy is slightly greater than the binding energy, the probability for absorption is highest.”

Goldstein et al. [48] also provide an equation to describe the attenuation of x-rays passing through a material. They show that:

$$\frac{I}{I_o} = \exp \left[ -\left( \frac{\mu}{\rho} \right) \rho \delta \right]$$

(4.4)

where \( I \) = X-ray intensity after passing through a material,
\[ I_o = \text{X-ray intensity before entering a material,} \]

\[ \frac{\mu}{\rho} = \text{Mass absorption coefficient of a material (m}^2/\text{kg),} \]

\[ \rho = \text{Material density (kg/m}^3 \text{), and} \]

\[ h = \text{Distance penetrated by beam (m).} \]

The mass absorption coefficient for a material depends upon the element which generated the x-ray and the specific x-ray from that element which is being absorbed. Since the most energetic x-ray producible with a 60 kV accelerating voltage is a tungsten K\(\alpha_1\) x-ray and since most vacuum chambers are constructed of 304 stainless steel, an attempt was made to find a mass absorption coefficient for \((K\alpha_1)_W\) in Fe. Despite extensive search of the literature, this data does not appear to be readily available [48, 198, 199].

Experiments at F.E.P. indicated that 4 mm of lead would be sufficient to cut emitted x-ray intensities by more than half and that 8 mm of lead would ensure operator safety. Examination of comparative x-ray attenuation data presented by Schiller et al. [11] indicated that for a 60 kV e-beam source, approximately 1.15 cm of steel would provide an equivalent amount of x-ray protection as 4 mm of lead. Thus, a safe chamber wall thickness was calculated to be 2.30 cm, and, after adding a small additional factor of safety, a stainless steel chamber wall thickness of 2.54 cm was specified.

In addition, viewing ports to permit direct observation of the evaporation process had to be covered with x-ray absorbing glass to protect observers of the process. The required glass thickness also had to be calculated. A search for x-ray absorbing glass found that Perkin-Elmer (Minneapolis, MN) manufactured x-ray shielding glass with a 25% lead content. Using the F.E.P. data for pure lead, 1.6 cm of this lead glass was deemed sufficient to absorb all generated x-rays. The glass was available in 0.64 cm thick pieces, and so three pieces were used to cover each window.
The processing chamber was manufactured by GNB Corporation (Hayward, CA), and once the DVD system was put into operation, x-ray emissions from the chamber were checked and monitored using a hand-held detector. While the detector did confirm that the chamber wall thickness and viewport glass specifications were sufficient to prevent x-ray emission from the system (i.e. no signal detected above background radiation), leaks were detected around the thin walls of the flange ports on the chamber, around the edge of the processing chamber door, through the exhaust flange leading to the processing chamber pump, and through the aluminum gate valve separating the medium vacuum pumping system from the gun. The flange port leaks and the medium vacuum pumping system leak were eliminated by wrapping them with lead tape. Future chamber designs should not have the flange ports extend from the side of the chamber. Instead they should be mounted flush with the thick chamber wall. All gate valves used on future systems should be made of stainless steel. Leaks around the door and through the large pump flange were eliminated by mounting additional stainless steel inside the chamber to absorb the x-rays. Improved chamber design at the outset, in consultation with F.E.P., could have eliminated x-ray leaks associated with the system.

4.2.2. The chamber could accommodate various sources and substrates

As initially envisioned, the DVD system should have the ability to employ several carrier gas streams either simultaneously or sequentially to deposit a variety of materials. Fig. 4.6 shows a setup using three jets where two use an inexpensive resistance heater to evaporate less reactive / low melting point metals just beyond their nozzle’s exit. Although only one source, an e-beam source, is installed as a part of this dissertation research, the vacuum chamber was constructed with three ports for vapor source insertion (See Appendix A for exact port positions.). This multisource configuration increases the number of materials
which could potentially be deposited via DVD. For example, in a conventional e-beam evaporation system, alloys containing elements with widely varying vapor pressures (e.g. Ti-Mg or Ti-Nb alloys) cannot be deposited stoichiometrically from a single evaporation source, and use of multiple crucible sources to accomplish the task can be quite inefficient (c.f. Fig. 2.1) [11]. In a DVD system, higher alloy materials utilization efficiency could be achieved by directing all of the vapor from separate sources towards a rotating substrate. These separate material sources could utilize different carrier gas jets and evaporation means (Fig. 4.6). (It is also conceivable that a single e-beam, scanned between the two or more material sources, could generate neighboring vapor streams which could be mixed and carried to the substrate by a single gas flow.)
Additionally, the design of the DVD system appears well suited for reactive compound deposition (Fig. 4.7). Use of the carrier gas jet as an integral part of the DVD material synthesis pathway makes reactive deposition a natural extension of pure metal vapor transport in an inert gas jet. Reactive elements can be introduced into the processing chamber as a portion of the primary carrier gas flow (See section 4.4.) or via another reactive gas injection system to reconstitute compounds decomposed during evaporation or to create new compounds with pure elements evaporated from the crucible. Such system flexibility considerably expands a DVD system’s material synthesis options (e.g., functionally graded materials). Heller describes in detail the means by which reactive gases can be introduced through an injection system as shown in Fig. 4.7 [200].

**Figure 4.7  Pathways for reactive material deposition in DVD.** Reactive gases can be introduced before or after the metal vapor stream enters the carrier gas flow.

### 4.3 Crucible

A significant advantage of electron beam evaporation is the ability to bring the heating source, electrons, directly into contact with the source material to be evaporated. This avoids the need to conduct energy into the source material from hot, potentially reactive / contaminating crucibles or resistively heated wires. E-beam heating also allows enough
energy to be supplied to the source material for the evaporation of high melting point (refractory) materials. E-beam heating of the source usually results in the formation of a vapor-emitting molten pool which must be contained and controlled so that the molten top of the source does not run down the side of the feed rod like wax down a candle. This can be accomplished by placing the source material inside of a water-cooled crucible which cools the edge of the rod-stock sufficiently to contain the molten pool of evaporant inside a solid well of its own material, avoiding reactive contamination of the evaporant pool by the crucible.

A 1.27 cm diameter feed rod was chosen based on the known e-beam power and scanning coil deflection capabilities (section 4.1). In addition, the top of the crucible was carefully designed for use in the DVD system to minimize disruption of the carrier gas flow during operation (Fig. 4.8). The thickness of the crucible’s rodstock containing wall was mini-

Figure 4.8  **DVD’s unique crucible design.** The crucible design minimizes carrier gas stream interference from the vapor source while ensuring proper water cooling and rod stock containment.
mized and raised above the main portion of the water-cooled crucible so as to present a minimum cross-section to the gas flow. Sufficient cooling to this exposed crucible region was ensured by machining the entire center section of the crucible from one cylindrical piece of copper placed directly in contact with chilled cooling water. (For detailed crucible design drawings, see Appendix A.)

The DVD system crucible was constructed by Strohecker, Inc. (East Palestine, OH) to allow a 1.27 cm diameter rod of source material to be fed continuously up through the center of the water-cooled, copper crucible. An Aerotech, Inc (Pittsburgh, PA) computer-activated motor (model 140SMP) and multitasking motion controller (Unidex 100) was located outside the chamber and used to push the source material up to the top lip of the crucible. The motor’s rotary action was fed into the processing chamber using a Ferrofluidic, Inc. (Nashua, NH) model SS250CFCB rotary motion feedthrough. The rotary motion of the motor and feedthrough were converted to a translational motion via a rack and pinion gearing arrangement inside the chamber, directly beneath the source rod (Fig. 4.9).

4.4 Gas System

In the DVD system, the evaporated source material will be entrained in an inert or reactive gas flow and transported towards a substrate. One of the major concerns associated with low vacuum processing, which was noted in the Background section, is potential contamination of deposited films as a result of the gas in the chamber. To ensure that pure material films could be created using DVD technology, a gas introduction system was designed to minimize the concentration of carrier gas born contaminants in the system (Fig. 4.10). In addition to ensuring that gas introduced into the system was pure, the gas system had to be capable of regulating the rate of gas flow through the system and controlling the gas pressure ratio between the mixing and processing chambers.
To ensure uncontaminated deposits, high purity (99.999% pure) compressed gas cylinders of helium or argon were selected as the initial source of the carrier gas introduced into the system. While this gas purity level is reasonably good, many applications require that moisture and oxygen contamination levels be reduced to the level of parts per million or parts per billion to ensure quality material creation [5]. Thus, after leaving the gas bottles, further cleansing of the gas flow was undertaken. From the compressed gas cylinders, the carrier gas was conducted through stainless steel tubing and into a continuously operating purification (gettering) system to reduce oxygen and moisture levels below one part per
billion and total impurity levels into the low parts per thousand million range. The Semi-Gas Systems (San Jose, CA) model L-2000 purifier utilizes beaded, porous, chemically stable organometallic polymers that irreversibly bind to a variety of vapor-phase impurities to produce a clean gas flow. At present a purification system has not been installed to remove moisture or other contaminants (e.g. carbon monoxide, carbon dioxide) from reactive carrier gases (e.g. oxygen).

Figure 4.10 **A schematic showing the DVD system configuration.** In the low vacuum DVD system, electron beam evaporated source material is transferred to a substrate by a directed gas flow entering the chamber through a nozzle.
Having established a means of gas purification, the rate of gas introduction into the system had to be precisely regulated so that repeatable experimental conditions could be established. To control gas flow rates, a parallel array of computer-activated mass flow control valves was inserted into the gas feed line of the DVD system. The mass flow control valves and their accompanying multigas controller were purchased from MKS, Inc. (Andover, MA) since this system allowed up to eight flow valves to be regulated through one controller. Although only two flow valves were initially installed, additional flow valves for other (reactive) gases or for second and third evaporation sources could be installed in parallel at a later time if needed.

The flow valves were calibrated for helium and argon and monitored by a model 647B MKS multigas controller. Mass flow rates were determined within the flow valves by measuring the heat required to maintain an elevated temperature profile along a laminar flow sensor tube built in parallel to the main laminar flow of gas through the valve. For a specific flow meter range and gas species, flow is proportional to the voltage necessary to maintain a constant temperature profile. The MKS sensing technique uses three heaters to create a known temperature profile along the sensor tube, and then maintains that profile during gas flow by means of an auto-balancing bridge circuit [201]. Argon and helium are sensed identically by the flow valves due to their similar thermal conduction properties, and thus combinations of the two gasses from a precisely mixed compressed gas cylinder can be passed through the flow valves and simultaneously regulated. The two valves installed for use with the e-beam evaporation source can control up to 10 standard liters per minute\(^1\) (slm) and 200 slm of gas flow respectively. While the 200 slm valve (model 1562A) is rated to control flows as low as 3 slm, its flow control at this level was found to fluctuate too much to provide constant experimental flow conditions, necessitating parallel

\(^1\) standard liter - one liter of any gas at atmospheric pressure and room temperature.
Installation of the 10 slm valve (model 1259C) for use in low gas flow experiments. Installation of this second flow valve made possible the precise control of gas flows as low as 0.1 slm.

After purifying and regulating the gas flow through the DVD system, an additional mechanism had to be incorporated into the system design to allow variation of the pressure ratio between the mixing and processing chambers (Fig. 4.10). As explained in section 2.2.3., the ratio of gas pressures between the mixing chamber and the processing chamber controls the carrier gas jet velocity as it travels through the processing chamber and interacts with the substrate. An ability to change carrier gas velocity could correlate to changes in vapor transport and deposition characteristics affecting material property development. While fluid dynamics studies [116] have shown that the velocity in the throat of the nozzle can be at most sonic (Mach number, \( M = 1 \)), the carrier gas accelerates to a higher Mach number and velocity, as predicted by equations (2.19) and (2.20), upon entering the processing chamber if flow at the throat is choked\(^1\). The maximum flow velocity attained depends upon the exact pressure ratio reached in the system.

In the DVD system (c.f. Fig. 4.10), two subsystem components were added to the gas flow system to make possible variation of the carrier gas velocity. To change the mixing chamber/processing chamber pressure ratio, either nozzles can be attached to the end of the gas flow tube leading from the mixing chamber into the processing chamber or a variable position throttle plate, located between the processing chamber and the main system vacuum pump, can be opened and closed. The nozzles allow the gas flow tube to be reduced from a maximum diameter of 2.2 cm. The mixing chamber / nozzle assembly was

---

\(^1\) choked flow - the type of fluid flow that occurs through a minimum area region (i.e. a nozzle) where the pressure ratio (mixing chamber / throat) is greater than or equal to that given by substituting \( M = 1 \) into equation (2.19).
designed by Hill [202], based upon design concepts presented in Fox and McDonald [116], and built by MDC (Hayward, CA). The nozzles designed for the system were straight orifice nozzles designed by Ratnaparkhi [203] as opposed to specially designed converging or converging / diverging nozzles. The variable position throttle plate was manufactured by GNB Corporation (Hayward, CA).

4.5 Vacuum Pumps

Critical to the proper operation of the DVD system are the vacuum pumps which maintain the proper vacuum levels in the e-beam gun and pull the carrier gas through the processing chamber at the necessary rates. Pumps for the high vacuum and medium vacuum portions of the e-beam gun were selected based upon pumping capacity specifications supplied by F.E.P. The chamber pumping capacity required to create a supersonic jet for a nozzle diameter up to 2.2 cm in chamber pressure between 1 Pa and 650 Pa (~0.01 - 5 Torr) was determined by Hill [202] using isentropic flow calculations (Appendix A).

In the DVD system constructed for this dissertation, the e-beam gun employs a differentially pumped gun column to generate an electron beam in a $10^{-8}$ Pa pressure zone evacuated by a Balzer (Hudson, NH) TPH330 double flow standard turbomolecular vacuum system in series with a Varian (Lexington, MA) SD300 roughing pump (total capacity = 22,200 l/min @ $10^{-7}$ Pa). Once created, the electron beam is transmitted with minimal energy loss down the gun column into a $10^{-4}$ Pa pressure region evacuated by an Edwards High Vacuum, Inc. (Poughkeepsie, NY) Model EH500 mechanical booster pumping package (a Roots type blower) in combination with an Edwards Model E2M80 (total capacity = 8500 l/min @ $10^{-4}$ Pa) direct drive, sliding vane type vacuum pump. Finally, the beam emerges into the evaporation chamber through the hole in the replaceable tungsten plug where experimental pressure conditions are maintained by a Stokes (Philadelphia, PA)
Model 1722 (total capacity = 30,000 l/min @ 10^{-2} Pa) blower package (a Model 412H11 rotary oil-sealed pump in combination with a Model 615-1 positive displacement, dry, high-vacuum booster).

### 4.6 Vacuum Gauges

Correct reporting of the vacuum pressures in the mixing and processing chambers of the DVD system is critical for assessing and controlling the vapor-phase material synthesis capabilities of the DVD system. These pressures and pressure ratios determine the Mach number and velocity throughout the carrier gas flow, process parameters likely to affect material property development. To ensure accurate pressure measurement in the mixing and process chambers, the three gauges mounted in this portion of the system were chosen to be gas independent capacitance manometer gauges which allow various process gases to be utilized during film synthesis without gauge recalibration. The two gauges on the mixing chamber and gas inlet tube are Leybold-Inficon (L.I.) model CDG100 vacuum gauges (East Syracuse, NY) while the gauge on the processing chamber is an Edwards High Vacuum, Inc. model 622AB. All three gauges can read pressures between 1 Pa and 10 KPa (~10^{-2} and 100 Torr). While the L.I. capacitance manometer gauges provide accurate readings at or near room temperature, the Edwards gauge guarantees accurate readings at gas temperatures up to 200°C (temperatures possibly generated by the DVD process and heater lamp warming of the gas).

In addition to the three gauges mounted on the mixing and process chambers, three more pressure measurement gauges mounted on the e-beam gun helped ensure proper gun operation by allowing pressures in the differentially pumped lower gun region and the high vacuum filament region to be monitored. E-beam gun specifications dictate that the vacuum level in the high vacuum portion of the system be better than 6.0 \times 10^{-4} Pa (~5 \times 10^{-6}

Torr) for proper bolt and wire cathode operation (section 2.1.3.). Pressure in this region is monitored using a L.I. thermocouple-type vacuum gauge (model TR901) in concert with a L.I. cold cathode vacuum gauge (model 850-610-G2). The dual gauge arrangement is required by the cold cathode gauge’s inability to operate at atmospheric pressure. Instead, it must be activated by the pressure reading of the thermocouple gauge after pressure in the high vacuum portion of the system drops below $1.9 \times 10^{-2}$ Pa ($\sim 10^{-4}$ Torr). The cold cathode gauge can read pressures as low as $1 \times 10^{-5}$ Pa ($\sim 10^{-7}$ Torr). Monitoring pressure in the gun is important to prevent damage to the gun or contamination of the filament as described in section 2.1.3. The two most likely reasons that the pressure in the high vacuum portion of the gun could be too high are that the cross-valve separating the high-vacuum region from the rest of the system has been opened before the processing chamber has been evacuated to processing pressure levels (0.001 - 5 Torr) and that the 2.5 mm hole in the tungsten plug at the bottom of the gun has been eroded and enlarged by excessive contact with the e-beam. Pressure in the medium vacuum portion of the gun is checked using another L.I. thermocouple gauge (model TR 901). The thermocouple gauge can read pressures as low as $1 \times 10^{-2}$ Pa. Readings from all six gauges were monitored by two L.I. digital readouts, models CM3 and CC3, capable of reading three gauges each and of being easily interfaced with a computerized data acquisition system.

4.7 Substrate Temperature Control System

As noted in Chapter 2, substrate temperature can be critical to the development of desired material properties. To provide flexibility in adjusting the temperature of the substrate, the DVD system was equipped with a temperature control system consisting of up to four Research, Inc. (Minneapolis, MN) heaters (model 5305-02) in combination with a power supply (model 609), an Omega (Stamford, CT) model CN76000 temperature controller,
and an Omega type J thermocouple. Each heater lamp has the rated ability of projecting 10 kW/linear meter onto a substrate 3.81 cm in front of the lamp. In a chamber without moving gas, these lamps could heat a substrate in excess of 1100°C. However, for gas flows between 1 and 20 slm, experiments in the flowing gas DVD system showed that properly tuned lamps could heat a flat metal substrate to just above 600°C.

4.8 Computer Control Methodology

The Directed Vapor Deposition system described in this dissertation represents a fairly sophisticated material synthesis tool comprised of numerous complicated subsystems. The individual monitoring and control of each subsystem was not deemed to be a safe or user friendly mode of system operation. In addition, centralized computer control was identified as a way to facilitate data collection and minimize the number of consoles which had to be monitored, allowing the system operator to concentrate upon the experiment in progress. Development of a central operator / system interface was deemed critical to efficient system operation. Thus, every effort was made during system design to choose equipment (e.g. vacuum gauges, gas controllers, motor controllers, e-beam gun controller) which would make possible computer control of the DVD system.

Equipment manufacturers offered either serial or parallel interfaces for computer-based system monitoring and control. Both interfaces have strengths and weaknesses. Serial interfaces (e.g. RS-232, RS-485) can be hardware intensive since they must have a dedicated cable and interface unit installed in the control computer so that the computer knows from which device the signal is coming. If the control computer has a limited number of interface board “interrupts” available, the complexity of the system which can be controlled is limited. However, if sufficient hardware is available, serial connections can make possible rapid monitoring and control since the host computer does not have to
determine which device is transmitting data. It already knows which system component sends information to each dedicated serial board.

Parallel interfaces (e.g. IEEE-488.2 or GPIB) represent a more sophisticated communication interface since the IEEE standard specifies that all transmissions over its interface should include five bits of address information. This allows a total of thirty two \(2^5\) devices to communicate over one interface line and computer interface board (i.e. 1 computer plus 31 external devices). While this arrangement decreases the amount of hardware necessary for system interfacing, it limits control speed somewhat since address information must be sent with each signal and only one system component can send along the cable at any given time. Table 4.2 records the communications specification for each major piece of control equipment in the DVD system. For the current DVD system, the desired sampling rate was only about 1 sample / second, a rate sufficiently slow to make the IEEE-488 system configuration attractive.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Manufacturer</th>
<th>Model</th>
<th>Interface Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron Beam Gun</td>
<td>F.E.P.</td>
<td>HPE 10/60</td>
<td>RS-232</td>
</tr>
<tr>
<td>Gas Flow Controllers</td>
<td>MKS</td>
<td>647B multigas controller</td>
<td>IEEE-488</td>
</tr>
<tr>
<td>Vacuum Gauges</td>
<td>Leybold Inficon, Edwards High Vacuum</td>
<td>CM3 or CC3 digital readout</td>
<td>IEEE-488</td>
</tr>
<tr>
<td>Source Feed Motor</td>
<td>Aerotech</td>
<td>Unidex 100 multitasking motion controller</td>
<td>IEEE-488</td>
</tr>
<tr>
<td>Heater Lamps / Thermocouple</td>
<td>Omega</td>
<td>CN76000 Temperature Controller</td>
<td>RS-485</td>
</tr>
</tbody>
</table>

In addition to the selection of hardware for computer / DVD system interfacing, a user / computer software interface also had to be selected. DVD system control was carried out
using National Instruments’ LabVIEW™ software version 3.0 running under MS Windows v.3.11 on a Gateway2000 486 CPU / 66MHz computer with 24 Mb of memory. LabVIEW™ allowed creation of a graphical user interface (GUI) from which the system operator can specify the file to which to save experimental run data, set gas flows, change e-beam powers, dictate motor actions, and observe real time graphs of pressure versus time data helpful in monitoring each experimental run (Fig. 4.11). Behind the GUI, Lab-

![Figure 4.11](image)

**Figure 4.11** The **graphical user interface developed for the DVD system.** The LabVIEW™ front panel makes possible centralized DVD system monitoring, data acquisition, and open-loop control.

VIEW™ provided an object-oriented programming environment in which flow chart type
objects were connected by visual wires to form the necessary data acquisition and control algorithms rather than typing in traditional lines of computer code (Fig. 4.12).

Figure 4.12 Object-oriented programming for the DVD computer interface. This portion of the LabVIEW™ code monitors the user interface for changes in the desired gas flow through one of the mass flow controllers. If the user makes a change, the code sends the new value to the multigas controller which opens or closes the mass flow control valve to obtain the new flow level.

While the DVD system user can supply e-beam power setting information through the LabVIEW™ interface, the actual control of the e-beam gun occurs through an IBM PC compatible, 386 CPU computer and associated hardware dedicated to monitoring gun performance. Functions of this computer include ensuring that the cross-valve separating the high vacuum portion of the gun from the rest of the system is open, adjusting the power of the e-beam focussing electromagnets and executing a beam direction checking routine every time beam power is changed. The direction routine monitors the amount of current hitting the gun nozzle and anode and minimizes that current flow, thus ensuring that most
of the beam’s electrons are flowing out through the 2.5 mm hole in the bottom of the gun and into the processing chamber. If the nozzle or anode currents become excessive, the control computer automatically reduces the beam power to its lowest possible level while it attempts to correct the problem by varying the strength of the e-beam positioning coils. Once low nozzle and anode current readings are achieved (i.e. the beam is passing through the hole in the bottom of the gun), beam power is cycled back to the setting established through the LabVIEW™ front panel. The usual cause of a high anode current is an improperly assembled Wehnelt cup assembly. The most likely cause of an excessively high nozzle current is beam spreading caused by use of incorrect beam focussing currents (Fig. 4.3) or too high a chamber pressure. Once the strength of the electromagnetic field in the focussing coils is adjusted or the chamber pressure is reduced, beam spreading will diminish and the majority of the beam will pass through the opening in the bottom of the gun, allowing material synthesis to resume.

4.9 Concluding Remark

Having constructed the e-beam powered Directed Vapor Deposition system (Fig. 4.13), experiments could now be conducted and models of vapor transport developed to evaluate the system’s performance and to provide insight into how changes to the system’s process variables affected vapor transport in the system, particularly vapor adatom distribution, deposition efficiency, kinetic energy, and angle of incidence.
Figure 4.13 The assembled DVD system in the laboratory. This photograph shows the DVD system after all major components were assembled. To the right are the central control computers and hardware and the e-beam power supply. Behind the processing chamber and e-beam gun in the central portion of the picture are the vacuum pump for the lower portion of the gun (left) and the processing chamber vacuum pump (green).